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RUBBER CHEMISTRY AND TECHNOLOGY

Rubber Chemistry and Technology is published quarterly under the supervision of the Editor representing the Division of Rubber Chemistry of the American Chemical Society. The object of the publication is to render available in convenient form under one cover all important and permanently valuable papers on fundamental research, technical developments, and chemical engineering problems relating to rubber or its allied substances.

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NEW BOOKS AND OTHER PUBLICATIONS

ELASTIC AND CREEP PROPERTIES OF FILAMENTOUS MATERIALS AND OTHER HIGH POLYMERS. By Herbert Leaderman. Published by the Textile Foundation, National Bureau of Standards, Washington, D. C. 7 x 10¼ in. 278 pp. $2.00.—In an effort to understand better the nature of the mechanical and electrical properties of high polymers, and how they are related to chemical constitution, much work has been done in the past decade on the physics of high polymers. This current work is concerned with a study of a phenomenon —delayed elasticity—which is observed in most high polymers. The second part of the book gives an account of experiments that have been carried out by the author at M. I. T., under the auspices of the Textile Foundation, on the creep and creep recovery behavior of rayon, nylon and silk filaments. The experimental results are interpreted in terms of the structure of these materials, and conclusions are drawn concerning the mechanism of elastic and plastic deformation of textile filaments. The first part of the book deals with similar work that has been carried out with other high polymers, including rubber, and contains a critical discussion of relevant theories and of previous experimental work on delayed elastic behavior in other materials, such as glass. This book, in presenting some of the current concepts concerning the structure and mechanical behavior of filamentous materials, should be of special value to the textile industry. For the same reason, however, it should also be in the hands of all those who are concerned with the manufacture and processing of plastics and rubberlike materials. The book has an extensive bibliography and a cross-referenced subject index. [From *The Rubber Age* of New York.]

THE WEEPING WOOD. By Vicki Baum. Published by Doubleday, Doran & Co., Inc., Garden City, N. Y. 5¾ x 8½ in. 531 pp. $3.00.—The whole long, tragic and sometimes romantic story of rubber is told in this new book by the celebrated author of "Grand Hotel". It is told in the guise of a novel, which is actually three or four novels in one, since Miss Baum tells it in terms of people—what people did to rubber and, more particularly, what rubber did to people. The history of rubber from the time its first commercial possibilities

were recognized through the controversies which marked the launching of the emergency synthetic rubber program in the United States is covered. Following the technique which has marked her previous works, the author depicts the story of rubber as witnessed by fictional creatures. We become acquainted with the atrocities which marked the beginning of rubber collection activities in South America through the eyes of Ambrosio, a Branco from Ceara; witness the cultivation of seedlings in London's Kew Gardens through Daniel Chalmers, young botanist who originally prized his orchids more than the rubber seeds; follow the seedlings to Ceylon with young Daniel and watch his moral standards fall apart as his rubber trees grow in stature; learn of the development of bud grafting in Sumatra as told by Piet Gruytgens; trace the growth of large tire companies in the United States through the career of George Tyler, so-called rubber baron; sit in on the start of the labor movement in Akron, as told by an ex-soldier; learn of the attempted sabotage of the German synthetic rubber program by an anti-Nazi; listen to a Senate investigation of patent arrangements between Usa Oil and I. G. Farbenindustrie; and, finally, share the promise that rubber will be returned to the Western Hemisphere and will be made to "sing on wheels". With the whole world for her background, rather than the confines of a small hotel, Miss Baum has told a vivid, panoramic story. From the standpoint of a novel, it makes interesting reading, particularly for those who can take grimness in wholesale doses, since the story of rubber, especially in its early days, is filled with evil and greed. But the book is intended to be more than just another novel. According to its preface, it "contains as much fact as it contains play and make-believe; it endeavors to give not only entertainment but also a certain amount of information; thus, it is an emulsion, a hybrid, a mongrel". Unfortunately, some of the so-termed facts are decidedly inaccurate. If nothing else, Miss Baum is positive in her assertions. In telling of the transportation of rubber seeds from Brazil to Kew Gardens, she stamps Sir Henry Wickard as a smuggler. True, this is the popular concept, but it has often been argued that the seeds were taken with the full knowledge and consent of the Brazilian Government. Only a few years back, this latter version was given a semi-official backing by Brazilian authorities, based on the discovery of some documentary evidence. Again, telling the story of Charles Goodyear through one of his numerous creditors, she intimates that Goodyear was not the real discoverer of vulcanization; "he just put one over on Nathaniel Hayward". Still again, in her chapter covering the Senate investigation, a counterpart of that launched into the actual Standard Oil-Farbenindustrie cross-licensing agreement, she leaves no doubt that the oil company was entirely at fault and bordered the line of treason in its dealings with the German chemical trust where synthetic rubber was concerned. When the author gets into the story of synthetic rubber, then errors pop up one after the other. For instance, her description of metallic sodium is a chemical joke; Buna-S formulas included are incorrect; the statement is made that butadiene and styrene can be made from almost any hydrocarbon; Chemigum and Ameripol are called Buna-S types of synthetic rubber; Neoprene is termed unsatisfactory for tires. These are only some of the inaccuracies; there are plenty of others. All in all, however, Vicki Baum's saga of rubber is well told, with rubber made both hero and villain. Because of its background it should prove especially interesting to members of the rubber industry, hundreds of whom are now helping to write the history which may some day become the background for a novel of the future. [From *The Rubber Age* of New York.]

THE CHEMICAL FRONT. By Williams Haynes. Published by Alfred A. Knopf, 501 Madison Ave., New York 22, N. Y. 5½ x 8½ in. 264 pp. (plus index). $3.00.—Writing in his usual clear, concise style, Mr. Haynes, one-time publisher of *Chemical Industries*, has furnished an interesting and dramatic story of the chemical munitions of modern warfare, of the men who discovered them, how they were made and used, and what they promise. Explosives, smoke screens, poison gas, sulfa drugs, serums and vaccines, blood plasma, atabrine, synthetic rubber, light metals, plastics, high-octane gasoline—all these pass in review, with comments from an individual who has watched many of them from laboratory to commercial state. The story of synthetic rubber is told in a chapter entitled, "Chemistry in Politics". First relating the history of synthetic rubber from the identification of isoprene by Williams in 1860, the author then discusses the current government production program. He outlines the confusion which surrounded the start of this gigantic endeavor and then tells of the trials and tribulations of William Jean in trying to have Washington recognize the importance of "Jeanite" rubber. In concluding this chapter, he predicts that synthetic rubber is here to stay and is ready to challenge natural rubber for one of the world's greatest commodity markets. The book has 18 chapters and a subject index. It is liberally illustrated, including 8 plates in full color. [From *The Rubber Age* of New York.]

MONSANTO CHEMICALS FOR THE RUBBER INDUSTRY. Monsanto Chemical Co., Rubber Service Department, Akron, O. 30 pages.—This bulletin contains specifications, general information, and a number of suggested applications of twenty-one accelerators, five antioxidants, and other materials such as wetting agents and deodorants. Included also is information on organic colors for rubber produced by the Federal Color Laboratories, Inc., for which Monsanto is the sole selling agents. The data on most of the accelerators and antioxidants include suggested typical applications based on parts per hundred of natural rubber, Buna synthetic rubbers, and for natural rubber latex. General instructions for use and the classification of accelerators and antioxidants according to strength, type, and specific advantages are given. [From the *India Rubber World.*]

PVA—PROPERTIES, USES AND APPLICATIONS. R. & H. Chemicals Dept., E. I. du Pont de Nemours & Co., Inc., Wilmington, Delaware. 8½ x 11 in. 8 pp.—The general properties, uses and applications of PVA—polyvinyl alcohol—are discussed in this technical bulletin, with emphasis on the latter. The specific applications in the paper, leather and cosmetic industries are outlined, with brief reference made to general applications, including adhesives, protective films, molded products, extruded products, emulsions, gloves, insecticides, and photographic films. A table showing the effect of various solvents on the physical properties of extruded PVA tubing compounds is included. [From *The Rubber Age* of New York.]

CARE AND MAINTENANCE OF COMBAT TIRES. B. F. Goodrich Co., Akron, Ohio. 8½ x 11 in. 48 pp.—This booklet represents Section I of the Goodrich U. S. Army Training School Manual, which has now been made available for general distribution. It provides information on the proper care, preventative maintenance and servicing of tires, tubes, endless and block tracks and other rubber products of a military nature, such information being of the utmost importance to Army men operating motorized equipment. A second

section on the care and maintenance of endless rubber band tracks for half-track vehicles will be made available shortly. [From *The Rubber Age* of New York.]

ELECTRIC INSTRUMENTS: PRINCIPLES OF OPERATION. (GET-1173). General Electric Co., Schenectady, N. Y. 8 x 10½ in. 20 pp.—This new publication presents a concise discussion of the characteristics of electric instruments, what makes them operate, and the individual limitations of the various types. It is pointed out that the use of electricity in manufacturing processes has become so general that the important question of whether it is being used in the most economical way is sometimes overlooked. It is suggested that a study of the construction and application of electric instruments invariably points the way to lower costs and improved manufacturing methods. [From *The Rubber Age* of New York.]

SLIDE RULE SIMPLIFIED. By Charles O. Harris. Published by American Technical Society, Drexel Av. at 58th St., Chicago, Ill. 5½ x 8¼ in. 266 pp. $2.50. ($3.50 with special slide rule, not sold separately.)—Although slide rules are indispensable tools to the engineer and scientist, who use them constantly during their daily work, it is held in awe by many others who could well profit from its use, such as estimators, merchants, accountants, manufacturers and many business men. One of the primary aims of this book is to dispel the idea that the slide rule is difficult to master and replace it with the certain knowledge that anyone who will study and practice can learn to use the slide rule with ease and confidence. The book contains many pictorial views of the slide rule, and points discussed are clearly indicated. Explanation of all steps include every figure or calculation necessary to obtain the desired results. A decided feature is the section added to most chapters which shows the basis or fundamental principles for and of all slide rule functions. There are 14 chapters, plus a comprehensive subject index. [From *The Rubber Age* of New York.]

RUBBER, POLYISOPRENES, AND ALLIED COMPOUNDS

IV. THE RELATIVE TENDENCIES TOWARDS SUBSTITUTIVE AND ADDITIVE REACTION DURING CHLORINATION *

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Although the established mode of reaction of chlorine with unsaturated systems is primarily additive, it has recently been shown by Groll and his collaborators that, under suitable conditions, substitutive reaction may not only occur but may become the major reaction, to the exclusion of addition. According to these authors, high temperatures in the range of 300–600° seemed generally to be necessary if substitutive reaction is to predominate, but subsequently it was shown by Rust and Vaughan[2] that a considerable degree of substitutive reaction can be realized at temperatures in the range 130–200°, provided certain catalysts which produce free radicals in contact with the halogen are present.

The polyisoprene system has been found to be particularly susceptible to substitutive attack by oxygen[3], and it has long been known that, judged by the quantity of hydrogen chloride liberated, the chlorination of rubber proceeds largely by substitution in the earlier stages of reaction[4]. The character of the products thus produced and the influence of the experimental conditions on the course of reaction were not, however, studied in any detail by McGavack.

Since the production of hydrogen chloride in the treatment of an olefinic substance with chlorine is no certain indication that true substitution has occurred, new experiments have been made with the object of examining further the character of reaction in the case of rubber and of olefins of allied type. In these experiments attention has been given to the influence of light, oxygen, and temperature on the course of reaction. To avoid, as far as possible, complication due to the formation of olefin hydrochlorides through the addition of some of the liberated hydrogen chloride to the olefin, steps have been taken to remove all hydrogen chloride formed in the reaction rapidly from the reaction vessel by means of a stream of inert gas; also the reaction has been conducted at as high a temperature as possible, since the rate of absorption of hydrogen chloride by rubber solutions appears to decrease as the temperature is raised[5]. The upper limit of temperature has, unfortunately, been much restricted by the necessity of using solvents which will both dissolve rubber and remain unattacked by chlorine at their boiling points, but even at the comparatively low upper limit thus enforced (77°), it is believed that there is little risk of the undesired hydrochloride-formation occurring.

Conditions of reaction.—To ensure homogeneous chlorination of rubber, it has been necessary to work with solutions of the hydrocarbon. The only readily available solvent suitable for use with rubber was carbon tetrachloride which had been freed from disulfide. Chloroform was used in some experi-

* Reprinted from the *Journal of the Chemical Society*, July 1943, pages 289–296.

SUMMARY OF CHLORINATION EXPERIMENTS WITH RUBBER

Expt. No.	Solvent	Conditions: Light	Conditions: Atmosphere	Conditions: Temp.	Chlorine reacted, mols. per C_5H_8	HCl formed, mols. per C_5H_8	Substitutive reaction %	Product: Cl %	Product: I.V.	Product: [η]††
1	CCl_4	near-dark	N_2	77°	0.81	0.787	97	30.0	175	...
2	$CHCl_3$	"	"	62	0.90	0.884	98	30.4	163	...
								28.2	(insol. portion) 44% of whole	
3	$CHCl_3$	"	"	62	1.84	<1.65	<88	49.1	42.5	...
								40.0	(insol. portion) 44.5% of whole	
4	CCl_4	"	"	77	1.61	1.16	72	52.8	41.5	...
5	$CHCl_3$	dark	"	62	1.02	0.988	97	33.9	154	...
								27.1	(insol. portion) 24% of whole	
6	CCl_4	"	"	77	1.00	0.973	97	33.6	140	0.416
7	CCl_4	"	"	77	1.85	1.29	70	...	...	...
8	CCl_4	light	"	77	0.83	0.806	96	29.3	173	...
9	CCl_4	dark	"	77	1.07	0.998	94	...	...	...
		"	"	77	0.54	0.184	34	...	...	...
		light	"	77	0.65	0.340	52	...	...	...
10	CCl_4	dark	"	77	1.07	1.038	96	...	...	...
		light	"	77	1.01	0.499	49	...	...	...
		"	"	77	0.58	0.614	100	...	...	...
		"	"	77	0.29	0.318	100	...	...	...
					2.95	2.469	84	64.6	0	...
11	CCl_4	"	"	77	1.12	0.973	86	...	...	...
		"	"	..	0.46	0.201	44	...	...	...
		"	"	..	0.50	0.338	67	...	...	...
					2.08	1.512	72	58.2	0	0.755††
12	CCl_4	near-dark	N_2 with trace of O_2	77	1.04	1.012	98	...	...	...
13	CCl_4	"	much O_2	77	1.0	0.960	96	35.2	117	...
14*	CCl_4	"	N_2	77	0.86	0.830	96.5	...	...	insol.
15†	CCl_4	"	"	77	1.04	1.030	99	...	...	insol.
16	CCl_4	"	"	−30	1.0	0.822	>82	34.2	129	1.93
17‡	none	"	vac.	−80	0.58	0.230	*ca.* 40	35.9	118	...
18	CS_2	"	N_2	−80	1.0	0.671	67	34.4	...	...
19	CCl_4 + HOAc	"	"	80	0.98	0.921	94	...	...	...
20§	CCl_4	"	"	77	1.18	0.986	84	42.9	...	1.04
21§	CCl_4	"	"	77	1.0	1.00	100	33.8	...	...
22‖	CCl_4	"	"	77	0.67	0.626	93	27.2	...	...
23**	CCl_4	"	"	77	0.96	0.876	91	37.5	...	1.23
24	CCl_4	"	"	77	0.15	0.147	98	6.75	317	...
25	CCl_4	"	"	77	0.27	0.259	96	12.3	250	...

* Quinol present. † Phenyl-β-naphthylamine present. ‡ Dry crepe rubber employed. § Crepe rubber employed. ‖ Milled crepe rubber employed. ** Gel rubber employed. †† Intrinsic viscosity in benzene + 15% methanol, except that No. 12 was in benzene alone.

ments, but proved to undergo substitution too readily to be satisfactory, for, although in the reaction vessel the rubber became chlorinated preferentially to the solvent, yet in the condensing and absorbing systems some chlorination of the solvent vapor carried from the reaction vessel by the effluent gas occurred—especially when the operation was conducted in light—so giving fictitiously high values for the degrees of substitution attained. The chlorinations, except where the influence of oxygen was under examination, were carried out in strict absence of air, in the apparatus described on p. 10.

Course of reaction.—The results obtained under various conditions are summarized in the table, multistage chlorinations being regarded as single

experiments and so appearing under one number. If it be assumed that all the hydrogen chloride produced during chlorination arises by substitutive reaction (and the validity of the assumption is considered later), it can be categorically stated as the result of the experiments that, for all reactions occurring in darkness or in light and at temperatures in the neighborhood of 80°, the dissolved rubber is attacked wholly substitutively by chlorine, $^{-}C_5H_8^{-} + Cl_2 = {}^{-}C_5H_7Cl^{-} + HCl$, and this applies as long as the first molecule of chlorine per C_5H_8 unit is being consumed. After this stage additive reaction becomes recognizable (see Experiments 10 and 11), and proceeds side by side with substitutive reaction until a second molecule of halogen per C_5H_8 unit has been consumed. When a third molecule of chlorine is brought into reaction (see Experiment 10), the process becomes again exclusively substitutive and proceeds with increasing difficulty. Nevertheless, up to the stage represented by the interaction of 2.95 moles of chlorine per C_5H_8 unit, 84 per cent of the chlorine is found to have reacted substitutively. With regard to the uniformity or heterogeneity of reaction during the consumption of the second molecule of chlorine, Experiment 11 indicates that there is some slight, but not very marked, tendency for the additive reaction to be greater during the consumption of the first half molecule than during that of the second. The reaction product at the stage when slightly more than 2 moles of chlorine per C_5H_8 group have reacted at 77° is a tough solid containing 58.2 per cent of chlorine, saturated to iodine chloride, and stable in air. The wholly substituted products obtained by reaction of 1 mole or less than 1 mole of chlorine per C_5H_8 group are still somewhat rubberlike, and are stable when kept in evacuated tubes; when, however, they are exposed to air, they evolve hydrogen chloride and become transformed into hard resinous masses with no rubberlike properties. When carbon tetrachloride is replaced by chloroform as solvent, much the same course of reaction seems to be pursued, but its details cannot be observed very accurately, owing to complications arising from chlorination of the solvent vapors (see above) and from the unavoidable separation of some solid chlorinated material which has a lower chlorine content than the product remaining in solution.

The course of reaction as determined by the quantity of hydrogen chloride evolved may, therefore, be approximately represented up to the stage at which 3 moles of chlorine have combined with each C_5H_8 group by the following equations, in which the double isoprene unit is used to avoid introducing half atoms:

$$C_{10}H_{16} + 2Cl_2 = C_{10}H_{14}Cl_2(Cl, 34.6\%) + 2HCl$$
$$C_{10}H_{14}Cl_2 + 2Cl_2 = C_{10}H_{13}Cl_5(Cl, 57.2\%) + HCl$$
$$C_{10}H_{13}Cl_5 + 2Cl_2 = C_{10}H_{11}Cl_7(Cl, 65.4\%) + 2HCl$$

Elementary analyses of the products obtained in Experiments 10 and 11 agree closely with the requirements of these equations. Also various published carbon and hydrogen analyses for highly chlorinated rubbers[6] agree with regard to the C : H ratio with the formula $C_{10}H_{11}Cl_7$ now advanced, rather than with an earlier formula $C_{10}H_{13}Cl_7$ due to McGavack[4].

Influence of light and temperature.—The exclusively substitutive reaction occurring during the interaction of the first molecule of chlorine proceeds to all appearance with equal facility in darkness or in light[7]. It is concluded, therefore, that the substitutive type of reaction is in the main uninfluenced by light. The mixed reactions characterizing the interaction of the second mole

of chlorine appear to proceed in darkness or in light, but the reaction is accelerated by light. In the third stage the reaction is slow in the absence of light.

Variations due to change in the temperature of reaction have only been followed over moderate- and low-temperature ranges, since the paucity of suitable solvents has restricted observations (see p. 1). At 80° the course of the reaction described above is maintained, and no appreciable change in the dominant substitutive reaction is to be observed as the temperature falls to room temperature. At room temperature and below, however, some difficulty is experienced from a secondary reaction, due to the tendency of the liberated hydrogen chloride to combine additively with the rubber; nevertheless, it has been possible to show that, at temperatures as low as −30°, the reaction is still at least 82 per cent substitutive[8], and at yet lower temperatures, in spite of the fact that the additive reaction of chlorine becomes more pronounced, substitution is still important, amounting to at least 50 per cent at −80°. Chlorination proceeds very readily at these low temperatures, and it was even possible to bring to successful reaction a finely divided solid rubber[9], although here the product was not homogeneous.

The low-temperature chlorination products showed no sign of evolving hydrogen chloride when allowed to warm to room temperature, and indeed certain of the products[10] were raised to and maintained at 80° in the absence of air for one hour without any significant amount of hydrogen chloride being evolved. It seems unlikely, therefore, that at the higher temperatures chlorination proceeds by the addition of chlorine at the ethylenic linkages, followed by elimination of hydrogen chloride, thus simulating substitutive reaction, although in fact it is truly additive.

Influence of oxygen, antioxidants, and polarity of solvent.—Rust and Vaughan[2] have found that small proportions of oxygen catalyze the substitutive vapor-phase chlorinations of simple olefins at high temperatures, whereas larger proportions inhibit both substitutive and additive reactions—although, strangely enough, the liquid-phase chlorination of isobutylene was found to be exclusively substitutive and entirely unaffected by oxygen. In the case of rubber, the exclusively substitutive mode of reaction characterizing the interaction of the first molecule of chlorine remains unaffected, whether a trace or a substantial proportion of oxygen is mixed with the chlorine[11], but the products obtained when oxygen was present were of poor stability.

Similarly, the substitutive character of chlorination during the interaction of the first molecule of reagent was unaffected by the addition of the antioxidants quinol and phenyl-β-naphthylamine, but the products were again markedly unstable, and appeared to undergo a species of vulcanization, since, in contrast to the behavior of the chlorinated rubbers obtained when no antioxidants were used, they could not be redissolved after they had been isolated from solution. The vulcanizing action of quinol might well be due to the formation of a little tetrachlorobenzoquinone, which has a marked vulcanizing action on rubber[12], but its cause in the case of the amine is unknown.

Since Kemp[13] has indicated that the presence of glacial acetic acid is of assistance in suppressing substitutive reaction between iodine chloride and rubber, the influence of this polar solvent has been tested in the chlorination reaction of rubber. No more than a slight inhibitory action on substitution appears to accrue from the introduction of substantial amounts of acetic acid into the solvent used for the chlorination (carbon tetrachloride), since at 80° in near-darkness substitutive reaction to the extent of 94 per cent was observed. The product was again not very stable.

Influence of chlorination on molecular size.—When chlorine is passed into rubber solutions, a marked decrease of viscosity is commonly observed, probably owing to a reduction in the molecular weight of the rubber. Some quantitative observations have been made in collaboration with Dr. G. Gee, to whom the author's thanks are due. For this purpose the reaction product was isolated from solution, redissolved in benzene plus 15 per cent of methyl alcohol, and its intrinsic viscosity $[\eta]$ determined in dilute solution, as described by Gee[14]. It was found that samples of sol rubber having $[\eta] = 2.75$ passed, when chlorinated at 80°, to the point at which each C_5H_8 group had reacted with 1 mole of chlorine into "mono" chloro substitution products $(C_5H_7Cl)_n$, having $[\eta]$ of the order of 0.4. A sample of acetone-extracted crepe rubber of $[\eta] = 2.3$ gave a "mono" chloro substitution product of $[\eta] = 1.04$[15], and a sample of gel rubber ($[\eta]$ not measured but probably in excess of 2.5) gave a chlorination product[16] of $[\eta] = 1.23$. In the last two cases degradation was much less severe. The character of the degradation is not yet known with certainty, the phenomenon of molecular-weight reduction appearing not only as the normal and invariable result of autoxidation reaction[17], but also as a quite usual concomitant of reaction when a variety of reagents are employed with rubber. The apparent degradation effected by chlorine does not appear to extend beyond the stage of "mono" chloro substitution, and because in general the phenomenon appears most marked when the sol fraction of rubber is being employed, it seems likely that the phenomenon is an autoxidation effect arising from small concentrations of oxygen which are either already dissolved or incorporated (as peroxide groups) in the rubber, or gain access in spite of precautions during the preparation and subsequent manipulation of the reaction products. If this explanation is correct, it would be expected that the degradative effect would largely disappear if the chlorination of sol rubber were carried out at low temperatures, *i.e.*, under conditions which decelerate autoxidation, and this is observed in practice, since the "mono" chlorinated product has then $[\eta] = 1.93$. It is of interest that the "mono" chlorination of gel rubber, like that of sol rubber, seems to be substitutive, although the course of reaction is here obscured, owing to the rather high concentration of nonhydrocarbon substances in gel rubber.

The unsaturation of the chlorination products.—In the foregoing account the chief criteria of substitutive reaction have been the production of 1 mole of hydrogen chloride per mole of chlorine reacted, the analytical data, and the considerable thermal stability of additive chlorination products where these have been formed. Although there is no evidence to show that, under the conditions of reaction (especially the temperature range) adopted, there is any considerable production of hydrogen chloride by the secondary decomposition of previously formed, double-bond-addition products, a hypothesis of double-bond reformation by elimination of hydrogen chloride, either instantaneously as a concomitant of additive reaction of chlorine at a double bond, or from an activated dichloride, cannot be entirely rejected without information as to the precise position of the double bond in the chlorinated molecule. Rust and Vaughan[18] have shown that, although ethyl chloride is stable at temperatures exceeding 415°, yet at 280° in the presence of chlorine it undergoes considerable decomposition to give ethylene and hydrogen chloride. Hence some further check on the reality of the substitutive reaction is desirable. When, however, resort is made to observation of the changes which occur in the unsaturation of the rubber as chlorination proceeds, there is the perplexing discovery that, simultaneously with the liberation of hydrogen chloride, the unsaturation as

measured by the iodine value decreases progressively, and the decrease is sufficiently marked to indicate that (apparently) a very substantial degree of additive reaction has occurred. For instance, for substitutive reaction in which each monoölefinic C_5H_8 unit passes into C_5H_7Cl, the iodine value should decrease from 373 to 248, but in practice it falls to a value between 130 and 150. It is thus necessary to seek an explanation of the apparent partial

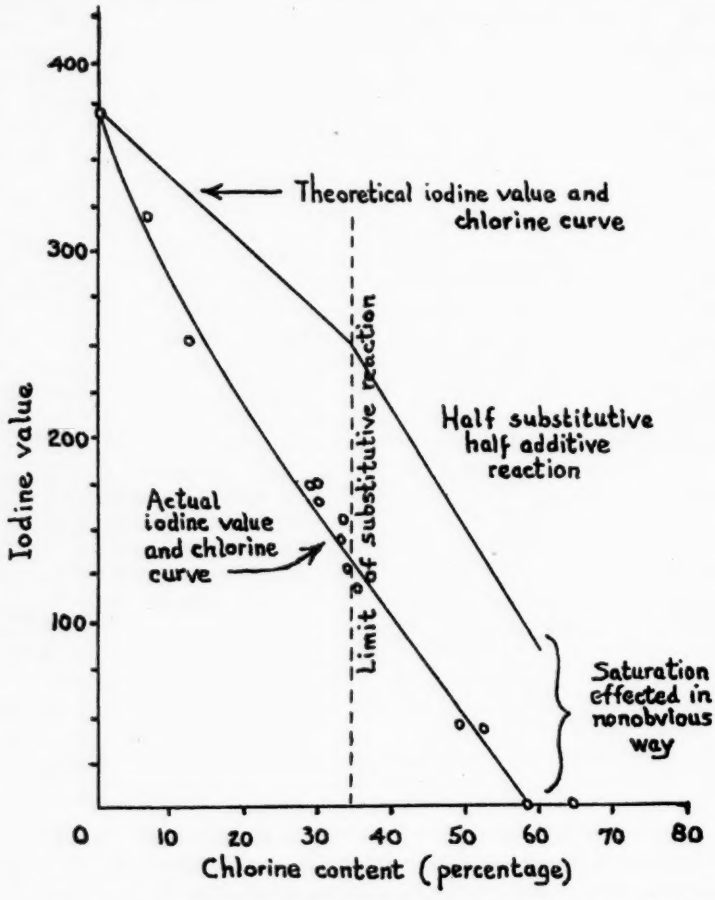


FIG. 1.—The relative tendencies toward substitution and additive reaction during chlorination.

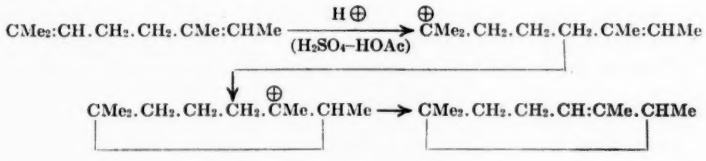
saturation of the chlorination products in terms of the invalidity of the iodine method of determining unsaturation as applied to chlorinated rubbers, or else in terms either of the occurrence of cyclization of the rubber chains due to chlorination, or of the inhibiting influence of the substituent chlorine atom in each C_5H_7Cl group on the reactivity of the double bond. An effect of the last type would fall in line with a vicinal effect of substituent chlorine reported by Rust and Vaughan[19], whereby the substitution of further chlorine atoms into the system $\rangle CCl \cdot C\langle$ is inhibited by the halogen already present, and with

the known low order of additive reactivity of iodine chloride to double bonds containing negative substituents, *e.g.*, dichloroethylene.

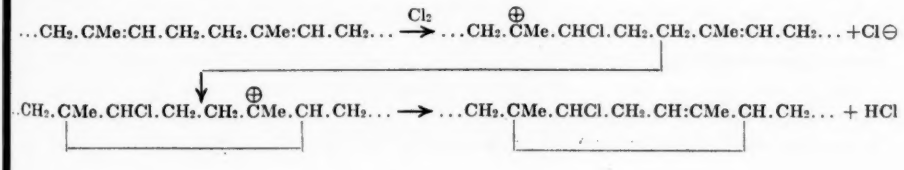
It should be stated that the iodine-value method (Kemp's procedure) has given over a long period results of the most admirable consistency in the determination of the unsaturation of polyisoprenes and other unconjugated polyolefinic systems. Variations in the time of reaction and in the proportion of iodine chloride employed have produced only minor changes in the iodine values observed, so that the above-mentioned anomaly is not to be traced to unsuitable experimental conditions. Peracetic acid, when used as a reagent for determining unsaturation, gave values for chlorinated rubbers substantially lower than those given by iodine chloride. It is, however, significant that when "mono" chloro-substituted rubbers $(C_5H_7Cl)_n$ reacted additively with further amounts of chlorine, they became saturated (to iodine chloride) at the expected points having regard to their initial unsaturation as determined by the iodine-value method. For instance, "mono" chlororubbers having the theoretical iodine value appropriate to their constitution (248) would be expected to add a whole molecule of chlorine per C_5H_8 group before becoming saturated, whereas "mono" chloro products having the commonly observed iodine value 124 should require adding only half a molecule. The latter requirement is found to be fulfilled in practice, since complete saturation (as measured by the iodine value) of the rubber halide was attained at a total chlorine content of 58.2 per cent[20] as the result of a combination of substitutive reaction with 1.5 moles and additive reaction with 0.5 mole of chlorine per C_5H_8 unit. During the interaction of the first molecule of chlorine per C_5H_8 group, *i.e.*, during the main substitutive stage, the observed iodine values soon began to fall below the theoretical values for homogeneous substitutive reaction; beyond this stage an undoubted additive reaction set in, the decrease in iodine value becoming more rapid. The relationship between chlorine content and iodine value is shown in Figure 1.

Cyclization as a cause of decreased unsaturation.—The ease with which the open-chain diisoprene, dihydromyrcene, cyclizes in presence of sulfuric acid-acetic acid is well known. One double bond in the diolefinic C_{10} unit is lost in this manner, and it is conceivable that reaction between chlorine and rubber could proceed in a comparable manner, *i.e.*, without definite $C_5H_8Cl_2$ units ever being formed. Possible mechanisms for these reactions are set out below:

(Scheme 1)



Scheme 2)



To examine this possibility, the behavior of 1-methylcyclohexene, dihydromyrcene ($\bar{|}_2$), and squalene ($\bar{|}_6$) towards chlorine has been investigated.

1-Methylcyclohexene may be regarded as a dialkyl derivative of monomeric rubber, $R \cdot CH_2 \cdot CMe{:}CH \cdot CH_2R$, and it is significant that the product obtained by interaction of the hydrocarbon at 80° with 1 mole of chlorine retains most of the original olefinic unsaturation and 0.79 mole of hydrogen chloride is liberated in its formation. The precise degree of unsaturation retained at the end of this stage amounts on an average to $\bar{|}_{0.76}$ per mole of the product, as determined by the iodine value; hence the overall reaction appears to be approximately 79 per cent substitutive, as shown by hydrogen chloride evolution and 76 per cent by iodine-value determination. The product is found, in fact, to consist mainly of chloro-1-methylcyclohexene admixed with a smaller quantity of 1-methylcyclohexene dichloride—the latter being a substance of considerable thermal stability. Hence, substitutive chlorination appears to be a major reactivity in the case of this olefin, but it is significant that the unsaturation of the monochloro substitution product appears to be somewhat lower (iodine value, 172) than that calculated (iodine value, 180), even when allowance is made for the presence of the dichloride found.

Dihydromyrcene (dimeric rubber) gives, in its reaction with 1 mole of chlorine, a mixed product, the formation of which is accompanied by the liberation of 0.82 mole of hydrogen chloride. This was found to consist mainly of unsaturated monochloro compounds (doubtless several isomeric compounds), from which a fairly pure *monochlorodihydromyrcene* could be isolated. Here, however, the difference between the observed and the calculated values for the unsaturation was more marked (*e.g.*, iodine value: found, 252; calculated, 284) than it was with 1-methylcyclohexene, and a still greater difference was found when 2 moles of chlorine reacted with dihydromyrcene, *i.e.*, 1 mole per C_5H_9 unit. In this case the total reaction product, formed with simultaneous liberation of 0.80 mole of hydrogen chloride, showed an average loss of unsaturation, measured by the iodine value of $\bar{|}_{0.28}$, and the pure *dichlorodihydromyrcene* isolated as the major reaction product showed an apparent loss of unsaturation of $\bar{|}_{0.22}$ (*e.g.*, iodine value: found, 190; calculated, 245). That this effect is due largely, though not entirely, to a cyclization mechanism is shown by reduction of the halide, whereby somewhat cyclized dihydromyrcene of iodine value 347 is obtained, whereas if the lowered unsaturation of the dichlorodihydromyrcene had been entirely due to cyclization, an iodine value of 285 would have been expected for the regenerated hydrocarbon.

Interaction of squalene with 0.85 mole of chlorine per C_5H_8 unit liberated hydrogen chloride in quantity corresponding to 90 per cent substitutive reaction, and the unsaturation of the total product, measured by the iodine value, fell considerably short of the calculated value (found, 184; calculated, 230). Reduction of the halide gave a somewhat cyclized hydrocarbon of iodine value 312 (theoretical value, 372).

The conclusions to be drawn are as follows. (1) Substitutive chlorination of 1-methylcyclohexene appears to proceed by a direct mechanism, since no question of cyclization arises here. (2) There is experimental indication that some degree of cyclization accompanies the chlorination of dihydromyrcene, and if this forms in fact an essential part of the chlorination-cyclization process represented in Scheme 2 (and is not merely a subsidiary and independent post-chlorination process due to the catalytic action of hydrogen chloride on the olefinic substance), it appears to be quite insufficient to account for more than a portion of the diminution in unsaturation observed to accompany chlorin-

ation. Hence there seems good ground for believing that the chlorination of dihydromyrcene is largely substitutive in character, and that the loss of unsaturation, measured by the fall in iodine value, is partly a real one to be attributed to cyclization, but partly an apparent one due to marked steric inhibition of iodine chloride addition at those double bonds which adjoin ·CHCl· or ·CCl_2· groups or which themselves form part of CCl=C groups. (3) In the case of rubber, chlorination is probably in the main truly substitutive, but the cyclization and the steric factor doubtless both play a part in causing the apparent reduction in unsaturation as measured by iodine value.

EXPERIMENTAL

Solvents.—Commercial carbon tetrachloride was purified by subjection to exhaustive chlorination in light in the presence of a trace of iodine, followed successively by washing with alcoholic sodium hydroxide, then with water, drying over calcium chloride, again chlorinating at the b. p. in light to destroy any trace of alcohol, refluxing over bleaching powder, washing, drying, and distilling over paraffin wax to remove hexachloroethane. The distillate was redistilled over mercury, and finally rectified through a good Widmer column. Thus purified, it gave on submission to chlorination at its b. p. in a nitrogen atmosphere only traces of hydrogen chloride. The chloroform and carbon disulfide employed were of "AnalaR" grade.

Rubber.—Except where otherwise stated, the rubber employed was sol rubber[21], $[\eta]$ 2.75, from which the most soluble (and most oxygenated) fractions had been rejected.

Nitrogen.—All nitrogen employed except in two experiments was commercial "purified" nitrogen, which had been thoroughly freed from oxygen by passage through Fieser's sodium hyposulfite solution[22].

Apparatus.—This is shown in Figure 2. The solution of rubber was placed in the flask *B*; the whole apparatus was then evacuated *via* stopcock T_3, and afterwards filled with purified nitrogen *via* stopcock T_1. A stream of nitrogen (entering through T_1) was kept circulating through the apparatus throughout the chlorination. The amount of chlorine required for use in any one experiment was condensed in the graduated tube *A*, and this was effected by connecting a chlorine cylinder and sulfuric acid wash-bottle to stopcock T_1, and applying solid carbon dioxide to *A*; meanwhile stopcock T_2 was closed to *B* and opened to the alkali trap *C*. As soon as sufficient chlorine was condensed, the cylinder was disconnected, and all uncondensed chlorine was swept out of the apparatus by a stream of nitrogen. Then T_2 was reopened to *B*, and the measured volume of chlorine in *A* caused to volatilize slowly into the rubber solution by allowing the temperature of *A* to rise gradually. The ebullition of the liquid chlorine and the removal from the latter of traces of dissolved oxygen were aided by passing purified nitrogen from a reservoir in which it was confined at 10 lbs. per sq. in. through a fine capillary jet inserted into *A*. Hydrogen chloride and unreacted chlorine in the effluent gases were absorbed in the system *D* (ice-cooled) containing 2 *N* sodium hydroxide.

Comparative experiments for determining the influence of light on the course of reaction were conducted in diffused sunlight, reinforced by the radiation from a 300-watt incandescent lamp, and in darkness; other experiments were made to test (separately) the influence of oxygen, antioxidants, polar liquids, and different temperatures of reaction.

Chlorination of rubber. General method.—The reaction procedure described above was used. For each determination of hydrogen chloride and unreacted

chlorine present in the absorption system *D*, the solution in the latter (containing chloride, hypochlorite, and excess of sodium hydroxide) was suitably diluted (to 500 cc.) and an aliquot part (25 cc.) titrated first with 0.1 *N* sodium arsenite to determine the hypochlorite present and to convert it into chloride. The total chloride was then determined by acidifying the resulting solution with acetic acid and diluting it to 100 cc., from which 10 cc. were taken for

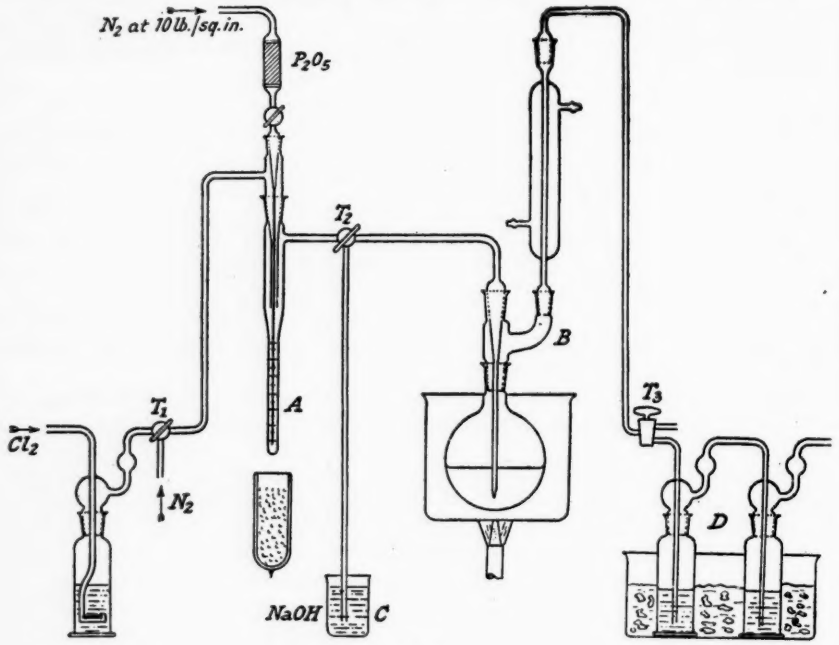


FIG. 2.

titration with 0.025 *N* silver nitrate, dichlorofluorescein being used as internal indicator[23]. The trustworthiness of the procedure was tested by a blank run in which no rubber solution was used: 2.66 grams (1.6 cc.) of liquid chlorine ($d^{-79°}$ 1.663) was vaporized into the chlorination vessel, so giving in the absorption system hypochlorite equivalent to 2.63 grams of introduced chlorine and total chloride equivalent to 2.62 grams of chlorine. No harmful effect due to traces of carbon tetrachloride which escaped into the absorption system was observed, but in a few experiments in which chloroform was used as solvent or in which somewhat volatile and hydrolyzable chlorination products were expected, the absorption system was slightly modified. In these cases two wash-bottles of water were used to absorb the hydrogen chloride, and a third, containing 2 *N* sodium hydroxide, to absorb the excess of chlorine. The small amount of free chlorine in the first two wash-bottles was determined by the arsenite method, and total chloride by the volumetric method as described above. The hypochlorite in the third wash-bottle was determined separately.

The chlorinated rubber was isolated from solution by precipitation into alcohol, and the adhering solvent removed at room temperature under reduced pressure (finally in a high vacuum). All chlorine contents were determined by the Carius method.

The essential details of the various experiments, not already covered by the table, are set out below. Generally, 5 grams of rubber in 300 cc. of solvent were used in the reaction flask.

Experiment 1.—This gave a soft, pale yellow, rubbery material; yield, 7.1 g. (found: C, 62.4; H, 7.6; Cl, 30.0; iodine value, 175; calculated for the substitutive reaction of 0.81 mole of chlorine: C, 62.5; H, 7.55; Cl, 30.0%; iodine value, 265). The product rapidly darkened on exposure to air and eventually became hard and dark brown, hydrogen chloride being liberated in the process; however, when stored in sealed evacuated tubes, it remained unchanged.

Experiment 2.—The reaction solution (red) contained a considerable amount of insoluble matter, which when separated formed a red solid (3.3 g.) having Cl, 28.2%. The solution yielded a soft, red, rubbery mass (4.2 g.) (found: Cl, 30.4%; iodine value, 163), unstable in air, turning yellow and liberating hydrogen chloride.

Experiment 6.—The product of reaction of 1 mole of chlorine per C_5H_8 group (7.2 g.) had Cl, 33.6; iodine value, 140 (calculated for C_5H_7Cl: Cl, 34.6%; iodine value, 248).

Experiment 10.—The final product of a chlorination conducted in four stages was a fine, white, stable powder (14.5 g.) having C, 32.1; H, 3.1; Cl, 64.6%; iodine value, 0; empirical formula $C_{10}H_{11.5}Cl_{6.8}$.

Experiment 12.—The nitrogen used in this experiment contained about 1% of oxygen. The product of reaction of 1 mole of chlorine per C_5H_8 group resembled that obtained in Experiment 6, except that the former was somewhat the less stable.

Experiment 13.—Here the nitrogen stream was replaced by a mixture of 60% of oxygen and 40% of nitrogen. The reaction solution was of lower viscosity than usual, and yielded a brown product containing no combined oxygen and of such poor stability that hydrogen chloride was liberated even in a vacuum (found: C, 57.7; H, 7.0; Cl, 35.3%; iodine value, 117).

Experiment 16.—Sol rubber (5 g.) dissolved in carbon tetrachloride (500 cc.) was placed in a flask fitted with a stirrer, dropping funnel, nitrogen inlet tube, and an outlet tube connected with the absorption system *D* shown in Figure 2. The rubber solution was cooled to −30°, and into the cooled solution 181 cc. of carbon tetrachloride containing 5.3 g. of dissolved chlorine were run as rapidly as possible, while the hydrogen chloride formed was swept into the absorption system by a brisk current of nitrogen. The reaction mixture (685 cc.) was poured into sufficient alcohol to give a total volume of 2 liters, of which 25 cc. were titrated with 0.025 *N* sodium hydroxide. The value of 82% substitutive reaction observed (cf. Table) must be regarded as a minimum, since the occurrence of some additive reaction between the hydrogen chloride formed and the unsaturated centers of the rubber cannot be excluded at the reaction temperature employed. The product formed under these conditions by the action of 1 mole of chlorine per C_5H_8 group was a soft, rubbery mass, similar to that obtained in Experiment 6, but more stable (found: Cl, 34.2%; iodine value, 129; $[\eta]$, 1.93).

Experiment 17.—Finely shredded crepe rubber was placed in a tube connected by a stopcock to a 2-liter reservoir, the whole being evacuated to 10^{-4} mm., and the stopcock closed. A tube of chlorine (5 g.) frozen in liquid air, and a flask containing 2 *N* sodium hydroxide, both fitted with stopcocks, were attached to the apparatus, which was again evacuated and sealed off. The tube containing the rubber was then immersed in solid carbon dioxide, and the

chlorine allowed to warm and vaporize therein. Under these conditions it was expected that any hydrogen chloride formed would, on account of its considerable vapor pressure at −80°, volatilize into the 2-liter reservoir, from which it could be periodically absorbed in the sodium hydroxide by momentarily opening the communicating stopcock. By operating in this way, a total of 2.02 g. of unreacted chlorine and 0.6 g. of chlorine as hydrogen chloride were absorbed, the remaining 3 g. of chlorine having reacted with the rubber, 42% substitutively. The figures thus obtained can be regarded as only approximate. There was no evidence of hydrogen chloride production when the chlorinated product was allowed to warm to room temperature; also, no free hydrogen chloride could be detected after the chlorinated product had been maintained at 80° for an hour. The product was a rather hard, stable substance, but not homogeneous, so the values given for chlorine content and iodine value in the table for this experiment are unlikely to be truly representative of the product as a whole.

Experiment 18.—Sol rubber (2 g.) dissolved in carbon disulfide (250 cc.) was placed in the apparatus used for Experiment 16, and cooled to −80°. A solution of chlorine (2.5 g.) in carbon tetrachloride (30 cc.) was then run in at −70° to −80°. Some insoluble matter at once separated, and some hydrogen chloride was formed. The reaction product was placed in alcohol which had been previously cooled to −80°, the precipitated material was transferred rapidly to more alcohol at −80°, and there manipulated to free it from residual hydrogen chloride, and finally the precipitate was placed in alcohol at room temperature before being freed from solvent at reduced pressure (finally in a high vacuum). The values obtained (cf. Table) pointed to the occurrence of at least 67% substitutive reaction. Only mere traces of hydrogen chloride were found in the alcohol in which the product had been placed at room temperature, and in the vacuum system either at room temperature or at 80°, thus indicating that no evolution of hydrogen chloride had occurred on warming the chlorinated rubber from −80° to 80°.

Properties of monochlororubber, $(C_5H_7Cl)_n$.—The substituted rubbers obtained by the action of 1 mole of chlorine per C_5H_8 group were generally soluble in benzene and chlorinated hydrocarbons, but the solubility decreased when the specimens were stored, owing to their gradual deterioration. In this deterioration small amounts of hydrogen chloride were liberated over long periods at room temperature, but no high proportion of chlorine was lost ($\gtrsim$0.6% of combined chlorine) when the specimens were heated for 5 hours at 70–80°. The products became more stable after they had been boiled with water, but in this process not more than 3% of combined chlorine was removed, and the products so treated were no longer soluble. Refluxing the products in benzene containing aqueous-alcoholic potassium hydroxide caused a similar diminution in the chlorine content.

On treatment with zinc in boiling benzene containing acetic acid, the products lost all their chlorine, giving a finely divided, insoluble powder resembling the products commonly formed from rubber by reagents such as stannic, antimony, ferric, and zinc chlorides.

Chlorination of dihydromyrcene. Experiment 26.—Chlorine (4.6 g.) was passed into dihydromyrcene (3.90 g.; iodine value, 364) dissolved in carbon tetrachloride (90 cc.) at the b. p. of the latter, the apparatus shown in Figure 2 and the modified absorption system described on p. 11 being used. There were found (1) unreacted chlorine, 0.73 g.; whence reacted chlorine = 3.9 g. (0.98 mole), and (2) chlorine as hydrogen chloride, 1.56 g., corresponding to

80% substitutive reaction. The reaction solution was made up to 100 cc., and 2-cc. portions were taken for direct determination of unsaturation of the crude reaction product (found: iodine value, 166; calculated for 80% substitutive reaction: iodine value, 182).

Experiment 27.—Chlorine (11.0 g.; 1.01 moles per C_5H_9 unit) was passed into dihydromyrcene (10.62 g.) in the absence of a solvent at 90–100°. All the chlorine reacted, giving 4.36 g. of hydrogen chloride, corresponding to 80% substitutive reaction. Distillation of the product gave 11 g. of fragrant liquid, b. p. 42–65° (0.05 mm.) and 6 g. of a less volatile residue which decomposed below its b. p. The volatile fraction on redistillation at 10^{-3} mm. yielded a small fraction, b. p. 35–46°, and a main fraction, b. p. 46–48°, which proved to be nearly pure dichlorodihydromyrcene (found: Cl, 33.1; iodine value, 202; calculated for $C_{10}H_{16}Cl_2$: Cl, 34.25%; iodine value, 245).

Experiment 28.—Chlorine (8.04 g.; 0.5 mole per C_5H_9 group) was passed into 15.62 g. of dihydromyrcene; 3.3 g. of the chlorine appeared as hydrogen chloride, so corresponding to 82% substitutive reaction. The fragrant liquid product was distilled at 0.2 mm., giving the fractions: (1) b. p. 35–42°, (2) b. p. 42–44°, (3) b. p. 44°, (4) b. p. 44–46°, (5) b. p. 46–48°, (6) a small residue. The fractions (2) to (4) were combined and redistilled at 15 mm., giving three fractions of b. p. <88°, 88–90°, and 90–92° severally. The middle fraction proved to be fairly pure *monochlorodihydromyrcene* (found: Cl, 21.4; iodine value, 252; $C_{10}H_{17}Cl$ requires Cl, 20.55%; iodine value, 294).

Experiment 29.—The formation of dichlorodihydromyrcene (Experiment 27) was repeated, freshly prepared dihydromyrcene (iodine value, 373) being used. The fractionated product gave *dichlorodihydromyrcene*, b. p. 48–50° (0.01 mm.) (found: C, 58.1; H, 8.1; Cl, 33.85; iodine value, 190; $C_{10}H_{16}Cl_2$ requires C, 57.95; H, 7.8; Cl, 34.25%; iodine value, 245. The corresponding additive product, $C_{10}H_{18}Cl_2$, would require C, 57.4; H, 8.7; Cl, 33.9%; iodine value, 123). Reduction of the product with zinc dust and glacial acetic acid at 50–60° gave dihydromyrcene, b. p. 56° (15 mm.) (found: C, 87.0; H, 13.0; iodine value, 347; calculated for $C_{10}H_{18}$: C, 86.9; H, 13.1%; iodine value, 373).

Chlorination of squalene. Experiment 30.—Chlorine (5.1 g.) was passed into a solution of squalene of $n_D^{20.6°}$ 1.4954 (4.68 g.) in carbon tetrachloride (90 cc.) at the b. p. of the latter, the apparatus shown in Figure 2 being used. There were found: (1) unreacted chlorine, 0.95 g., whence reacted chlorine = 4.15 g. (0.85 mole), and (2) chlorine as hydrogen chloride, 1.86 g., corresponding to 90% substitutive reaction. The chlorinated product was a viscous oil, which darkened on exposure to air with liberation of hydrogen chloride (found: Cl, 33.6; iodine value, 184; calculated for 90% substitutive reaction of 0.85 mole of chlorine: Cl, 32.8%; iodine value, 230). Reduction of the product with zinc dust and glacial acetic acid gave some distillable liquid and an undistillable residue. The former, $n_D^{20.6°}$ 1.4958 was a somewhat modified squalene of lower unsaturation than the original specimen (found: C, 87.5; H, 12.5; iodine value, 313; calculated for $C_{30}H_{50}$: C, 87.7; H, 12.3%; iodine value, 372).

Chlorination of 1-*methylcyclohexene. Experiment* 31.—Chlorine (6.25 g.) was passed into a solution of 1-methylcyclohexene [8.14 g.; iodine value, 278 (calculated, 265)] in carbon tetrachloride (20 cc.) at the b. p. of the latter, the apparatus shown in Figure 2 and the modified absorption system again being used. There were found: (1) unreacted chlorine, nil, whence reacted chlorine = 1.04 moles; and (2) chlorine as hydrogen chloride 2.74 g., corresponding to 79% substitutive reaction. The unsaturation of the total product was deter-

mined directly from an aliquot portion of the reaction solution (found: iodine value, 145; calculated for 79% substitutive reaction of 1.04 moles of chlorine: iodine value, 150). Distillation of the product gave (1) a little low-boiling material, (2) a fraction, b. p. 56° (15 mm.) (5 g.), and (3) a fraction, b. p. 50–70° (0.01 mm.), but principally 55–60° (0.01 mm.). The fraction, b. p. 50–70° (0.01 mm.), was saturated to permanganate and to bromine (iodine value, 12) and doubtless consisted of the addition product 1-methylcyclohexene dichloride. Fraction (2), on the other hand, represented a constant-boiling mixture of this with chloro-1-methylcyclohexene (7.5% of the former) (found: C, 63.5; H, 8.45; Cl, 28.3; iodine value, 172; calculated for $C_7H_{11}Cl$: C, 64.35; H, 8.45; Cl, 27.2%; iodine value, 193; calculated for 92.5% of $C_7H_{11}Cl$ + 7.5% of $C_7H_{12}Cl_2$: C, 63.3; H, 8.4; Cl, 28.3%; iodine value, 180). Reduction of the constant-boiling mixture (5 g.) with zinc and glacial acetic acid at 60–70° gave 1-methylcyclohexene, b. p. 109–110° (758 mm.) (2.3 g.), contaminated with a trace of chlorinated hydrocarbon (found: C, 86.65; H, 12.55; iodine value, 264; calculated for C_7H_{12}: C, 87.4; H, 12.6%; iodine value, 265), together with a chlorinated compound of b. p. 36–38° (0.01 mm.) (found: C, 69.3; H, 9.5; Cl, 21.1%; iodine value, 148).

A further sample of chloro-1-methylcyclohexene was obtained similarly, but without solvent being used during chlorination. This sample (b. p. 56° (15 mm.)) had Cl, 28.3%; iodine value, 174.

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[16] Probably wholly "mono" chloro-substituted as far as the rubber is concerned, but that cannot be fully demonstrated, owing to the considerable proportion of nonhydrocarbon impurities present.
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MACROMOLECULAR COMPOUNDS. CCCXII

HALOGEN DERIVATIVES OF RUBBER HYDROCARBONS *

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INTRODUCTION

It has been assumed by Kuhn[1] and by numerous other investigators[2] that the threadlike molecules of rubber are kinked or tangled, both in the solid state or in solution, like the molecules of other high polymers, because of free rotation of their carbon bonds. This characteristic configuration is represented schematically in Figures 1*a* and 1*b*. According to this view, the elas-

FIG. 1*a*.

FIG. 1*b*.

Examples of aggregations of threadlike molecules suspended in solution. Aggregations which have the general character exemplified in Figure 1*a* occur more frequently than aggregations which have the general character exemplified in Figure 1*b*.

ticity exhibited by rubber can be explained by assuming that the fibre molecules are straightened out when the rubber is stretched, and return to their original state when the rubber retracts on release of the stress. When they are straightened out in this way, the fibre molecules may arrange themselves in the form of a lattice. On this basis it is easy to account for the well-known fact that rubber crystallizes when stretched. Kuhn has pointed out also that the viscosity law for fibre molecules is in accordance with this kinking or entanglement of such fibre molecules.

Nevertheless, there are various well known facts which indicate that organic molecules of this type have a stable structure. Thus it is incorrect to assume, as Kuhn has done, that a single carbon bond is, in contrast to a double bond, capable of free rotation, for in each case a definite amount of energy is expended

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in the conversion of one form of molecule into another form[3]. Furthermore, the viscosity law is consistent only with the assumption that, when in solution, fibre molecules are present in elongated form, for fibre molecules of similar chain lengths but of different cross-sectional areas have the same viscosity constant, provided that their molecules are solvated to the same degree.

In view of these facts, one is led to the conclusion that molecules which differ in diameter must be of the same length[4]. If, on the contrary, it is assumed that fibre molecules are kinked and entangled, then it would be expected that this effect would differ greatly among differently substituted compounds having fibre molecules. Accordingly the substituents in these compounds would be expected to have an influence on the viscosity constant. Actually, however, this is not the case, as has been shown, for example, in work on cellulose derivatives[5].

The final solution of the problem of the form of molecules is of fundamental importance in judging the behavior of macromolecular substances, *e.g.*, in gaining an insight into the elasticity of rubber and of Buna types of synthetic rubber, and into the differences in elastic properties of these two types of product.

On the basis of the viscous properties of linear macromolecular substances, it might be concluded that there are two types of substances with fibre or threadlike molecules[6]. The first type comprises those with comparatively rigid fibre molecules, to which belong cellulose and polyesters, *i.e.*, substances which obey the viscosity law for fibre molecules. The second type comprises substances with fibre molecules which are not rigid, *e.g.*, polyvinyl derivatives and rubber, which are characterized by an increasing kinking or tangling of their fibre molecules with increase in molecular weight. With these various substances, the viscosity constants do not increase in proportion to the increases in the degree of polymerization, but show functional relations to the degrees of polymerization[7]; in fact, in any homologous polymeric series, the viscosity constant does not increase relatively so rapidly as does the degree of polymerization. However, the different behavior of these substances can be explained also by a branching of the fibre molecules, as has been proved to be true of polyesters through determination of their end groups[8]. This applies also to polystyrenes, branching in which is the more extensive the higher the temperature at which they are prepared[9].

With all these compounds, the K_m values and, therefore, the proportionality factors between the viscosity constant and degree of polymerization, are lower than the K_m values of low-molecular compounds with unbranched fibre molecules; in fact, the K_m values decrease with increase in the degree of polymerization. The K_m values of rubber and of Buna types of rubber also are too low; in fact, they are approximately one-half the values of low-molecular paraffins and of squalene. This is true also of polyvinyl derivatives[10]. In the case of Buna types, branching of the macromolecules has been proved by chemical reactions, as, for example, by ozone decomposition[11]. On the contrary, the same sort of chemical investigation of rubber indicates that the rubber molecule contains very long isoprene chains[12]. Since the K_m values of rubber are approximately the same as those of Buna, one is led to the conclusion that their macromolecules are in each case branched, and that macromolecules of rubber differ from those of Buna only in the character of this branching[13]. Buna has many short-chain branchings, whereas rubber and likewise balata and gutta-percha must have relatively few branchings, in the form of very long lateral chains. Accordingly a rubber molecule contains only

relatively few weak points, and so it has not been possible up to now to prove their existence by chemical means as, for instance, by ozone decomposition. It is still possible, however, to gain a further insight into the structure of the rubber molecule by comparative studies of the molecular weights, determined osmotically, and the viscosity constants of derivatives of rubber. In view of this possibility, a detailed investigation of the halogen derivatives of rubber hydrocarbon was undertaken, and the present paper describes the results of this work.

SQUALENE HEXAHYDROCHLORIDE

Up to the present time, the validity of the viscosity law has been investigated only for homologous and polymerically homologous series of hydrocarbons, esters and amines, in other words, for compounds of the same general structure, and with approximately the same specific gravities. Halogen derivatives have received little or no attention in this connection.

To obtain an idea of the differences between the K_m values of halogen derivatives and the K_m values of rubber hydrocarbons, as determined in the course of the work to be described, the K_m constants of analogous low-molecular substances of known structures, *viz.*, squalene and squalene hexahydrochloride[14], were first of all determined. According to the viscosity law, both these compounds should have the same viscosity constant if the solvation of the halogen atoms is the same as that of the hydrogen atoms.

TABLE 1

VISCOSITY MEASUREMENTS OF SQUALENE AND SQUALENE HEXAHYDROCHLORIDE IN DIFFERENT SOLVENTS AT 20° C

(Degree of polymerization = 6)

Compound	Solvent	C (g. per l.)	η_r*	$Z\eta$	$K_m \times 10^4$
Squalene	Toluene	34.33	1.0843	0.00246	4.10
		51.94	1.1350	0.00260	4.33
Squalene hexahydrochloride	Toluene	10.06	1.0334	0.00332	5.54
		9.00	1.0286	0.00318	5.30
		10.00	1.0329	0.00329	5.48
Squalene hexahydrochloride	Chloroform	10.00	1.0328	0.00328	5.46
		10.02	1.0329	0.00328	5.46
		9.82	1.0321	0.00327	5.45
Squalene hexahydrochloride	Tetrahydrofuran	10.71	1.0346	0.00323	5.38
		11.71	1.0371	0.00332	5.54

* With account taken of the specific gravity of the solution and of the solvents.

Actually, however, the viscosity constant of squalene hexahydrochloride is considerably higher than that of squalene, as is evident from the data in Table 1. It will be seen also that the two compounds do not have the same K_m values.

The reason for the higher viscosity constant of squalene hexahydrochloride is still unexplained, and it is therefore not possible to decide whether the form of the fibre molecules is influenced by the chlorine atoms or whether the halogen atoms are more highly solvated than the hydrogen atoms, and, consequently, whether the higher viscosity is to be attributed to this latter condition.

The viscosity constants of substances of different structures can be compared only if it is assumed that the states of solvation of the dissolved molecules and the specific gravities of the particular substances are the same, for the viscosity of a substance in solution does not depend on the specific gravity of the dissolved portion but on its volume. Since the specific gravity of squalene ($s = 0.86$) and that of squalene hexahydrochloride ($s = 1.1$[15]) are considerably different, it is necessary in this case to compare the viscosity constants of solutions at the same volume-percentage concentration. It then becomes a question of multiplying the Z_η value by the specific gravity, and then comparing the K_m constants calculated from the following equation:

$$Z_\eta \cdot s = K_m' \cdot P$$

The K_m' values of squalene and squalene hexahydrochloride obtained in this way differ from each other still more than do the values obtained when the specific gravities are disregarded, as is evident in Table 2.

TABLE 2

COMPARISON OF THE K_m CONSTANTS OF SQUALENE AND SQUALENE HEXAHYDROCHLORIDE IN TOLUENE, TAKING INTO ACCOUNT THE SPECIFIC GRAVITIES

Substance	S	$K_m \times 10^4$	$K_m' \times 10^4$
Squalene	0.86	4.2	3.6
Squalene hexahydrochloride	1.1	5.4	5.9

The same behavior is found in the case of esters of tetrabromostearic acid[16], which have higher K_m constants than those of the corresponding unhalogenated compounds when the constants are calculated from data obtained with solutions of the same volume-percentage concentration.

When polyprene and polybutadiene are converted into halogen derivatives by addition of hydrogen chloride or by substitution of chlorine, the K_m values of the former would be expected to increase. This increase is actually found to be true of polyvinyl chloride, in which case the higher the chlorine content the greater the increase in the K_m value over that of the starting material[17].

HYDROGEN CHLORIDE ADDITION PRODUCTS OF POLYPRENES

When in solution, the polyprenes, rubber, balata and gutta-percha[18] readily add hydrogen chloride and are transformed into the respective hydrochlorides, which in the dry state are solid, inelastic masses. These should have a chlorine content of 33.92 per cent[19]. In the investigation described in the present paper, hydrochlorides of rubber and of balata were prepared. To this end, rubber and balata were prepared fresh from the corresponding latices, in the hope that in this way products would be obtained with the least possible changes having taken place[20]. The crude products were separated from the latices and were freed of resins by means of extraction with acetone, in the absence of light and air. The hydrocarbons were then purified further by dissolving in chloroform or toluene, freed of oxygen[21], with exclusion of light and air, then centrifuging, and finally transforming them into their respective hydrochlorides by passing pure hydrogen chloride into the solutions. Even when generated in a Kipp apparatus, hydrogen chloride contains traces of oxygen, and therefore had to be freed of this impurity by mixing with hydrogen and conducting the mixture over a hot platinum contact. With this procedure and with the precautions mentioned, it was possible to obtain hydrochlorides free of oxygen. A balata hydrochloride which was prepared with unpurified

hydrogen chloride still contained 0.8 per cent of oxygen, and was, as proved in later investigations, considerably degraded.

To transform a polyprene completely into its hydrochloride, hydrogen chloride was passed in at 0–5° C for 40 hours, with agitation; the reaction product was precipitated by methanol; the precipitated product was dissolved in benzene; the solution was centrifuged (with addition of animal charcoal) to remove impurities, the hydrochloride was fractionally precipitated from the clear solution by acetone, and each of the individual fractions was purified by repeated precipitation. When prepared in this way, the hydrochlorides contained 3–6 per cent less chlorine than the calculated value (see Table 3);

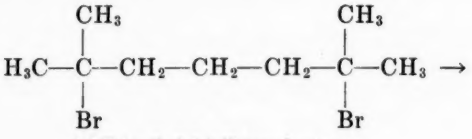
TABLE 3

ANALYSES[24] AND BASE MOLECULAR WEIGHTS OF POLYPRENE HYDROCHLORIDES[25]

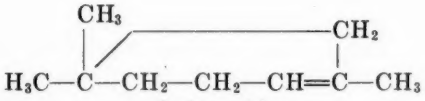
Product	Fraction	Carbon (percentage)	Hydrogen (percentage)	Chlorine (percentage)	Sum	Oxygen (percentage)	Base molecular weight (from Figure 2)
Calculated for $(C_5H_9Cl)_x$	..	57.47	8.71	33.92	...	...	104.5
Balata hydrochloride I	1	60.45	8.89	29.84	99.18	0.82	98
	2	...	...	28.77	...	...	97
Balata hydrochloride II	1	...	...	27.36	...	...	95
	2	63.13	9.41	27.58	100.12	...	95
	3	62.48	9.20	28.42	100.10	...	96
Balata hydrochloride III	2	64.87	9.54	25.52	99.93	...	92
Rubber hydrochloride IV	1	59.91	9.04	30.68	99.63	0.37	99
	2	...	...	29.61	...	...	98

hence they were only slightly unsaturated. The deficiency in the chlorine content is attributable to a secondary splitting off of hydrogen chloride, either during the preparation of the hydrochloride or during purification of the latter[22].

This cleavage of hydrogen chloride is accompanied by the formation of ring systems, *i.e.*, by cyclization[23], corresponding to similar observations on geraniolene hydrobromide, which is transformed into cyclogeraniolene, with splitting off of hydrogen bromide.



2,6-Trimethyl-2,6-dibromoheptane



α-Cyclogeraniolene

K_m VALUES OF POLYPRENE HYDROCHLORIDES

To get some idea of the K_m values, *i.e.*, the proportionality factors between the mean degrees of polymerization, $\bar{P}$, and the viscosity numbers, $\bar{Z}_\eta$, of the hydrohalides, the mean molecular weights, $\bar{M}$, were determined by the osmotic method[26], and then, by dividing by the base molecular weights, the mean de-

grees of polymerization, $\bar{P}$, were calculated. To estimate from Table 3 the base molecular weights of hydrohalides of different chlorine contents, a curve was constructed from calculations of the base molecular weights for different known percentages of chlorine. In this way it was possible, by graphical extrapolation, to estimate the base molecular weights of hydrohalides of various nonstoichiometric chlorine contents. These are recorded in Table 3 (see also Figure 2).

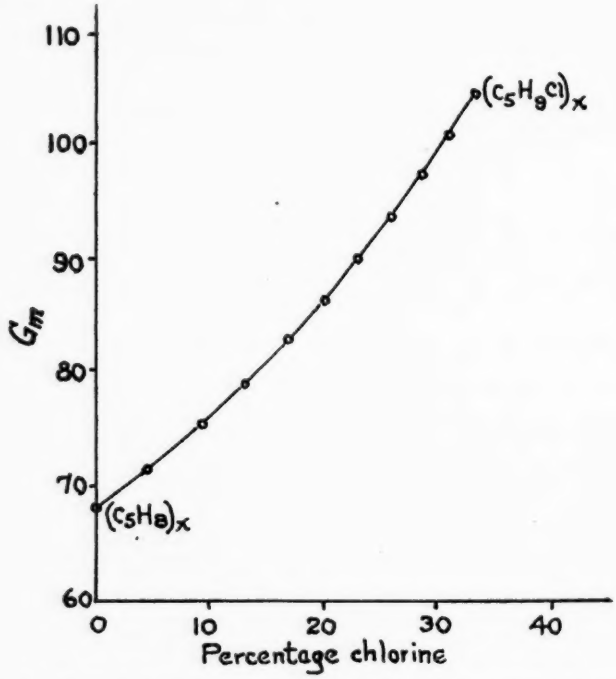


FIG. 2.—Change in the base molecular weight G_m of polyprene hydrohalides with increasing chlorine content.

In determining molecular weights by the osmotic method, Schulz cells were used[27]. As in the case of other linear macromolecular compounds[28], the p/c values were not constant, but increased with increase in concentration. The $\lim_{c\to 0} p/c$ values necessary for calculating the molecular weights were estimated by graphical extrapolation[29].

The osmotic measurements were carried out with toluene solutions at 27° C[30]. The viscosity measurements were carried out in an Ostwald viscometer, with toluene and chloroform solutions at 20° and at 60° C, *i.e.*, in solutions of low viscosities, or actually, relative viscosities below 1.20. From these measurements the viscosity constants (Z_η) were calculated. It was not necessary to determine the $\lim_{c\to 0} \eta_{sp}/c$ values, since in this range errors in viscosity measurements are less than 2.5 per cent[31]. The temperature factor, *e.g.*, the ratio: $\eta_{sp}60°/\eta_{sp}20°$, had an average value of 0.9 for this solvent, *i.e.*, of the same order of magnitude as has been found in general for macromolecular

compounds[32]. The K_m values calculated from the Z_η values and degrees of polymerization (determined osmotically) are shown in Table 4.

According to the viscosity measurements of squalene and squalene hexahydrochloride, it would be expected that the K_m values of polyprene hydrochlorides would be higher than those of the corresponding hydrocarbons. Actually, however, they are considerably lower, for the K_m value of balata was found to be 1.2×10^{-4} to 1.3×10^{-4}, and that of rubber[33] 1.7×10^{-4}. From this it may be assumed that, when hydrogen chloride is added, the elongated molecules of the polyprene are shortened, probably as a result of unidentified cyclization reactions, which take place in the transformation of the primary

TABLE 4

DETERMINATION OF THE K_m VALUES OF POLYPRENE HYDROCHLORIDES IN TOLUENE

Substance	Fraction	Chlorine (percentage)	G_m	$\bar{M}$	$\bar{P}$	$\bar{Z}\eta$	$K_m \times 10^4$
Hydrochlorobalata I	1	29.84	98	135,000	1,400	0.094	0.67
	2	28.77	97	51,000	530	0.042	0.79
Hydrochlorobalata II	1	27.36	95	380,000	4,000	0.168	0.42
	2	27.58	95	135,000	1,400	0.088	0.63
	3	28.42	96	45,000	470	0.032	0.68
Hydrochlorobalata III	2	25.52	92	105,000	1,150	0.088	0.76
Hydrochlorobalata IV	1	30.68	99	410,000	4,100	0.415	1.0
	2	29.61	98	140,000	1,450	0.187	1.3

hydrochloride with the calculated chlorine content into hydrochlorides with lower chlorine contents. In agreement with this, rubber hydrochlorides which have relatively high chlorine contents have also greater K_m values than those of balata hydrochlorides. The molecules of the former are, therefore, less cyclized than those of the latter. It should, furthermore, be noted that in all cases the K_m values decrease with increase in the mean degree of polymerization. In other words, high-polymeric substances are shortened to a relatively greater degree than are low-polymeric substances. The fact that the K_m values decrease with increase in molecular weight has been observed also in the case of most polyvinyl derivatives[34]. In addition to a shortening effect resulting from cyclization, there is, with polyprenes, a similar effect resulting from branching, a condition already present in the rubber molecule, as might be expected from the relatively small K_m values of the latter[35].

Hydrochlorides of rubber hydrocarbons can be conceived as chlorinated paraffin chains which carry in several positions extraneous groups in the form of branchings and unknown terpenelike rings. From the difference in the K_m values it must be concluded that the character and number of these extraneous groups in the various products may vary in some way, which has up to the present time not been explained.

ETHYLHYDRORUBBER AND ETHYLHYDROBALATA

OBJECT OF THE INVESTIGATION

The fact that a polyprene hydrochloride has a smaller K_m value than the K_m value of the polyprene from which it is derived can, as already mentioned, be attributed on the one hand to cyclization accompanying splitting off of hydrogen chloride. It may on the other hand depend on the fibre molecules

of polyprene hydrochloride being more strongly kinked than the fibre molecules of the hydrocarbon itself, as a result of the mutual attraction of the chlorine atoms, in accord with the views of Kuhn. If the latter is the case, straightening out of the macromolecules should take place when the hydrochloride is converted back into the polyprene hydrocarbon, and the resulting hydrocarbons should have the original, higher K_m values. On the other hand, if cyclization is responsible for the shortening of the molecules, the reconverted hydrocarbons must have a lower K_m value than do the original polyprenes, rubber and balata.

Among the numerous reactions[36] for splitting off chlorine from hydrohalides, only those which use organometallic compounds are of concern in the present discussion, because only these reactions take place under mild experimental conditions and at relatively low temperatures. It was hoped in this way to replace chlorine atoms by ethyl residues by reaction with zinc ethyl, with avoidance of side reactions which might alter the molecular forms. Since paraffins, squalene and hydrosqualene have the same K_m constants, the lateral methyl groups and the double bonds have no influence on these constants, and therefore it should be expected that ethylpolypranes would have the same K_m values as those of rubber and balata, provided that no cyclization reaction, involving shortening of the chains, takes place in the transformation of these polyprenes into their hydrochlorides.

PREPARATION OF THE PRODUCTS

The conversion of rubber hydrohalides into ethylhydrorubber by means of zinc ethyl has already been described[37]. Since the reaction is violent at room temperature, solutions of the polyprene hydrochloride in toluene were cooled to $-80°$ C, and zinc ethyl was added to the reaction mixture by breaking ampoules in the reaction vessel in an atmosphere of nitrogen. The reaction mixture was then allowed to rise to $-20°$ C during a period of 3–4 hours, was held at 0° C for 3 hours, and finally was raised to room temperature and, to complete the reaction, was warmed for 2 hours at 40° C.

In this reaction, ethane was evolved, an indication that chlorine atoms are split off from the polyprene hydrochloride as hydrogen chloride, and are not completely replaced by ethyl residues. The excess of zinc ethyl was decomposed at room temperature by addition of dilute hydrochloric acid, the toluene solution was extracted with dilute hydrochloric acid, and was washed with water to remove the zinc salts. The ethylpolypranes obtained in this way were precipitated by methanol, and purified by solution in toluene and reprecipitation by methanol. The hydrocarbons finally obtained in this way are completely ash-free and chlorine-free. According to analysis, these products contain higher percentages of carbon and lower percentages of hydrogen than the values for a quantitatively ethyl-substituted polyprane. They are weakly unsaturated to bromine. Hence in the conversion of polyprene hydrochloride by zinc ethyl, only a part of the chlorine is replaced by ethyl groups, while another part is split off as hydrogen chloride, with reformation of the double bond and cyclization.

The base molecular weight of these products, which depends on the degree of saturation, can be estimated by extrapolation of a curve representing the base molecular weight as a function of the hydrogen content of ethylpolypranes of definitely known compositions (see Figure 3). From the value of the hydrogen content determined analytically, the base molecular weight as a

function of the hydrogen content of ethylpolypranes of definitely known compositions (see Figure 3). From the value of the hydrogen content determined analytically, the base molecular weight can then be obtained, as shown in Table 5.

From the chlorine content of the polyprene hydrochloride and the hydrogen content of the ethylpolyprane it is possible, by graphical extrapolation, to

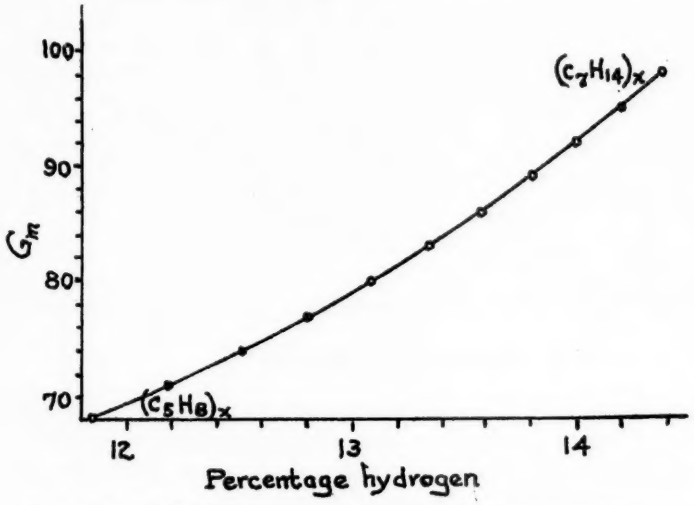


FIG. 3.—Base molecular weights of ethylpolypranes of different compositions.

TABLE 5

ANALYSES OF ETHYLPOLYPRANES

Substance	Carbon (percentage)	Hydrogen (percentage)	Base molecular weight (from Figure 3)
Rubber $(C_5H_8)_x$ (calculated)	88.15	11.85	68
Ethylhydrorubber $(C_7H_{14})_x$ (calculated)	85.63	14.37	98
Ethylhydrobalata I from hydrochlorobalata II 1	86.74	13.24	82
Ethylhydrobalata II from hydrochlorobalata III 2	87.13	12.78	77
Ethylhydrorubber III from hydrochlororubber IV 1	86.33	13.62	86

estimate how many C_5H_8 residues are present in the various products. These C_5H_8 residues are for the most part present in cyclized form, for both the polyprene hydrochloride and the ethylpolyprane are only slightly unsaturated.

According to Table 6, the percentages of C_5H_8 residues in ethylpolypranes are considerably higher than those of the corresponding polyprene hydrochlorides. In other words, the reaction with zinc ethyl, as already evidenced by the evolution of ethane, is characterized in every case by extensive splitting off of hydrogen chloride.

Table 6 also includes the mean degrees of polymerization of these products, obtained by osmotic measurements. These values show that the reaction of polyprene hydrochloride with zinc ethyl does not lead to polymerically analo-

gous ethylpolypranes, but that degradation to approximately one-half the original degree of polymerization takes place. In what manner this degradation of the macromolecules takes place is still uncertain. It cannot be attributed to attack by oxygen, by which polyprene is degraded extremely easily, because the last traces of oxygen are removed by zinc ethyl.

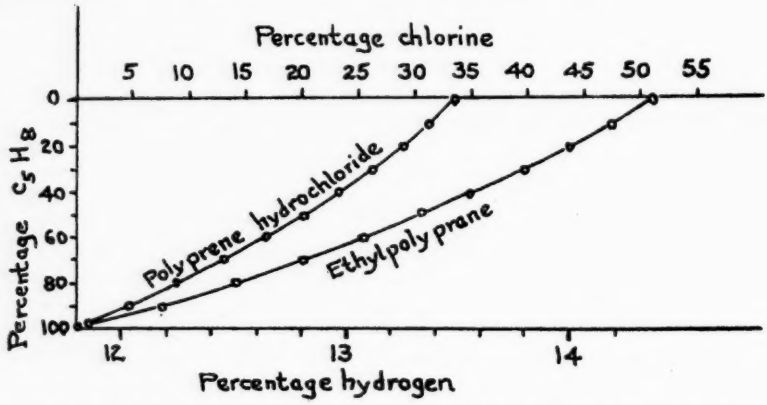


FIG. 4.—Estimation of the proportion of reformed C_5H_8 residues in polyprene hydrochlorides from their chlorine contents and in ethylpolypranes from their hydrogen contents.

TABLE 6

PERCENTAGES OF C_5H_8 RESIDUES IN POLYPRENE HYDROCHLORIDES AND THE CORRESPONDING ETHYLPOLYPRANES PREPARED FROM THEM
(See Figure 4)

Transformation	Chlorine (percentage)	Hydrogen (percentage)	C_5H_8 (percentage)	P
Hydrochlorobalata II 1	27.36		25	4,000
to ethylhydrobalata		13.24	55	1,200
Hydrochlorobalata III 2	25.52		35	1,150
to ethylhydrobalata II		12.78	70	650
Hydrochlororubber IV 1	30.68		15	4,100
to ethylhydrorubber III		13.62	40	1,900

K_m VALUES OF ETHYLPOLYPRANES

The average molecular weights of the ethylpolypranes prepared in the present work were measured in toluene solution by the osmotic method, and also were estimated by graphical extrapolation from the p/c values at various concentrations. From these molecular weights, the mean degrees of polymerization were calculated from the base molecular weights shown in Table 5. The K_m values were then obtained from the Z_η values, as shown in Table 7.

The K_m values of ethylpolypranes are, it is evident, approximately the same as those of polyprene hydrochlorides, or at least they are not essentially higher, and in no case are they so high as the K_m value of the original rubber hydrocarbon. Table 8 summarizes the changes in the K_m values accompanying the transformation of polyprenes into polyprene hydrochlorides and into ethylpolypranes.

TABLE 7

DETERMINATION OF THE K_m VALUES OF ETHYLPOLYPRANES IN TOLUENE

Substance	G_m	$\bar{M}$	$\bar{P}$	$Z\eta$	$K_m \times 10^4$
Ethylhydrobalata I	82	100,000	1,200	0.087	0.72
Ethylhydrobalata II	77	50,000	650	0.052	0.80
Ethylhydrorubber III	86	165,000	1,900	0.180	0.95

On the basis of these results, it may be concluded that the abnormally small K_m values of the polyprene hydrochlorides are not attributable to a shortening of the chains resulting from marked kinking of the molecules, for in no case was it found possible to obtain from the hydrochlorides a hydrocarbon with K_m value of the corresponding rubber hydrocarbon. A shortening of the chains, which is evidenced by abnormally small K_m values, is attributable therefore to a change in structure of the macromolecules of the polyprene as a result of cyclization reactions during transformation into the hydrochlorides.

TABLE 8

COMPARISON OF THE K_m VALUES OF POLYPRENES, POLYPRENE HYDROCHLORIDES AND ETHYLPOLYPRANES

Squalene →	squalene hexahydrochloride →	hydrosqualene[38]
4.2×10^{-4}	5.4×10^{-4}	4.5×10^{-4}
Balata[33] →	hydrochlorobalata II 1 →	ethylhydrobalata I
1.3×10^{-4}	0.42×10^{-4}	0.72×10^{-4}
Balata[33] →	hydrochlorobalata III 2 →	ethylhydrobalata II
1.3×10^{-4}	0.76×10^{-4}	0.80×10^{-4}
Rubber[33] →	hydrochlororubber IV 1 →	ethylhydrorubber III
1.7×10^{-4}	1.00×10^{-4}	0.95×10^{-4}

BROMOBALATA

In view of the experiments on addition products of polyprenes and hydrogen chloride, it seemed of interest to study an addition product of these hydrocarbons with a high halogen content. It is impossible to add chlorine solely to the double bonds of polyprenes, because it substitutes at the same time, and this secondary reaction cannot be avoided in the treatment with chlorine.

On the other hand, it is possible under carefully controlled conditions to add bromine to the double bonds; in fact this reaction has been utilized in the development of a quantitative method for determining rubber hydrocarbons[39].

TABLE 9

THE K_m VALUE OF BROMOBALATA

G_m	$\bar{M}$	$\bar{P}$	$Z\eta$	$K_m \times 10^4$
169	133,000	790	0.048	0.61

Nevertheless, in this case too, it has been found impossible to carry the reaction through quantitatively to completion. In the preparation of bromobalata, which was carried out with the usual precautionary measures, such as careful exclusion of oxygen and light, it was found that, even at the low temperature of 0° C employed, hydrogen bromide split off. The bromobalata, which was purified and fractionated by ordinary methods, had as a result a bromine content of only 56.16 per cent, whereas a true balata dibromide would contain

70 per cent of bromine. The K_m value, obtained both from osmotic measurements and from the viscosity constant, was of about the same order of magnitude as the K_m values of the hydrohalides of polyprenes.

Probably, therefore, in the formation of this addition product, the same reactions take place as in the case of addition of hydrogen chloride, *i.e.*, there is in each case a shortening of the chains, with formation of a cyclized product.

CHLOROPRENE

It was the object of further experiments to study the reaction of chloroprene with zinc dimethyl, for in this way it should be possible to obtain a hydrocarbon of the same composition as that of rubber, provided the reaction with zinc dimethyl proceeded in accordance with the following scheme.

CONVERSION OF CHLOROPRENE INTO A POLYMETHYLBUTADIENE

$$—CH_2CCl : CHCH_2CH_2CCl : CHCH_2— + Zn(CH_3)_2 \rightarrow —CH_2C(CH_3) : CHCH_2CH_2C(CH_3) : CHCH_2— + ZnCl_2$$

Under the conditions described in connection with ethylhydrorubber and ethylhydrobalata, chloroprene reacts with zinc dimethyl and zinc diethyl. There has, however, been no opportunity[40] to study the resulting hydrocarbons, and in the present paper only the initial experiments on chloroprene can be described

Like Buna and purified rubber, chloroprene[41] is extraordinarily sensitive to oxygen. To this may probably be attributed the fact that the soluble form of chloroprene is transformed into an insoluble form very easily on standing. In the case of rubber, it was proved that this transformation does not take place when both light and air are rigidly excluded. For this reason, the change from the soluble form into the insoluble form probably involves the formation of a network of long molecules through the agency of oxygen atoms[42]. Technical chloroprene was found to be only partially soluble in benzene. Chloroprene was precipitated from this benzene solution with the most rigid exclusion of air, and was purified by repeating this operation. As shown by analysis, this purified chloroprene had a low chlorine content and contained some oxygen.

TABLE 10

ANALYSIS OF CHLOROPRENE

Calculated from $(C_4H_5Cl)_x$		Found (percentage)		Base molecular weight (from analysis)
C	54.25	C	54.75	
H	5.65	H	5.67	88
Cl	40.10	Cl	39.09	
		Sum	99.51	
		0	0.49	

As with rubber, the osmotic measurements were carried out in the type of osmometer already described[43], with toluene (free of oxygen) as solvent at 27° C, in darkness. Only in this way was it possible to prevent degradation while the measurements were being made. The K_m value was calculated from the mean molecular weight, determined osmotically, and from the viscosity constant.

As may be seen in Table 11, the K_m value of chloroprene is of approximately the same magnitude as the K_m values of rubber (1.7×10^{-4}), of balata (1.3

$\times 10^{-4}$) and of Buna (1.5×10^{-4})[33]. The K_m value is, therefore, considerably higher than the K_m values of polyprene hydrochlorides. This is further evidence that the low K_m values of polyprene hydrochlorides are attributable to cyclization and not to the fact that the fibre molecules of the hydrochlorides

TABLE 11

THE K_m VALUE OF CHLOROPRENE

G_m	$\bar{M}$	$\bar{P}$	$Z\eta$	$K_m \times 10^4$
88	115,000	1,300	0.214	1.65

are, because of their chlorine atoms, kinked to a greater extent than are those of the hydrocarbons.

The experiments on chloroprene therefore confirm the conclusion, reached in the preceding section, that in this apparently simple transformation of rubber by hydrogen chloride, there is a considerable change in the structure of the molecule.

CHLORINATED RUBBER AND CHLORINATED BUNA

EARLIER VIEWS OF THE CONSTITUTION OF CHLORINATED RUBBER

It was to be expected that further light would be thrown on the problem of the constitution of the macromolecules of rubber by a study of chlorinated rubber, which is obtained by chlorination of rubber in solution. Chlorinated rubber is of considerable interest to the varnish industry because it gives hard, dense and weather-resistant coatings. The ordinary commercial products contain from 60 to 70 per cent of chlorine[44]. Chlorinated rubber is, therefore, not a chlorine addition product, *e.g.*, a rubber dichloride, which would have a chlorine content of only 51 per cent, but is a chlorine substitution product[44]. The primary addition product is extremely unstable, and at the very beginning of the chlorination reaction considerable evolution of hydrogen chloride is observed, even when the reaction is carried out in the cold.

The mechanism of the reaction has been explained by Nielsen[44]. The dichloride formed primarily splits off hydrogen chloride, with reformation of a double bond; chlorine then adds to this new double bond, and the process repeats itself. Chlorinated rubber is, therefore, a chlorine-substituted paraffin hydrocarbon. Theoretically a product with a chlorine content of 68 per cent might be regarded as rubber tetrachloride; but actually the chlorine is probably not distributed uniformly through the macromolecules. Accordingly chlorinated rubber is not only a mixture of molecules of different sizes but also is a mixture of molecules of somewhat different chemical structures. The mechanism of formation of chlorinated rubber makes it easy to understand why technical difficulties have been encountered so frequently in its production on a large scale. In the splitting off of hydrogen chloride, free radicals are formed transiently, and these can then unite with one another. In this way the whole reaction may, under the right conditions, be expended in the formation of a network structure[45].

In its behavior as a colloid, chlorinated rubber resembles a highly degraded, hemicolloidal rubber. Accordingly it was at first assumed that, in the chlorination of rubber, the labile carbon chains are subject to rupture, which can take place easily in the rubber molecule because of the allyl grouping of the double bonds[46]. Thus, for example, eucolloidal polystyrene is very easily degraded by the action of bromine in light[47]. Actually, however, as shown by

later experiments, the rubber molecule is degraded to only an insignificant extent during the formation of chlorinated rubber.

PREPARATION OF THE PRODUCTS

In the present investigation, technical grades of chlorinated rubber (Dartex and Tornesit (extra-high viscosity))[48] were used. These technical products were purified by solution and reprecipitation, were then fractionally precipitated from benzene solutions by the slow addition of ether, and the fractions were finally purified by repeating this procedure.

In further experiments, chlorinated balata was prepared by passing chlorine into a hot solution of 3 grams of balata in 300 cc. of carbon tetrachloride, while maintaining a current of carbon dioxide so that air would be completely excluded. The chlorinated balata was purified by adding animal charcoal, extracting with methanol, and further fractionating and purifying as was done with the technical grades of chlorinated rubber. It was found, in the course of the work, that chlorinated rubber and chlorinated balata can be prepared

TABLE 12

Substance	Fraction	Carbon	Hydrogen	Chlorine	Total	Oxygen	Base molecular weight (from Figure 5)
Dartex	1	...	...	62.92	...	...	180
	2	32.92	3.42	62.83	99.37	0.63	179
	3	...	...	63.81	...	...	184
Tornesit	extra-high viscosity						
	2	31.57	3.48	63.67	98.81	1.19	184
Chlorinated rubber prepared from SO_2Cl_2	1	37.78	4.03	57.28	99.09	0.91	158
Chlorinated balata	1	...	...	64.64	...	...	188
	2	31.73	3.54	64.83	100.10	...	189
Chlorinated balata prepared from SO_2Cl_2	2	39.70	5.16	54.90	98.76	1.24	150
Chlorinated Buna-85 (laboratory preparation)	2	30.99	3.23	64.79	99.01	0.99	150
	3	...	...	65.92	...	...	154
Chlorinated Buna-S (technical)	1	...	...	58.36	...	...	129
		37.05	4.25	57.18	98.48	1.52	126

also by the addition of sulfuryl chloride to solutions of rubber and of balata in carbon tetrachloride. Even at room temperature, the reaction is energetic, with evolution of sulfur dioxide. After boiling for 5 hours, the products were isolated and purified, as a result of which chlorinated rubber and chlorinated balata were obtained with 55–60 per cent chlorine content and with the same properties as chlorinated rubber and chlorinated balata prepared by passing chlorine directly into solutions of rubber and of balata.

In the course of this work on chlorinated rubber, an investigation was made also of chlorinated Buna. In these experiments, a technical product, a chlorinated Buna-S[49], was used. It was fractionated and purified in the same way as were the technical grades of chlorinated rubber. In still another experiment, chlorinated Buna was prepared by passing chlorine into a solution of Buna-85. In this preparation, there was obtained, in addition to a soluble portion, which was purified in exactly the same way as described for the preparation of chlorinated rubber, approximately the same yield of a portion which was insoluble

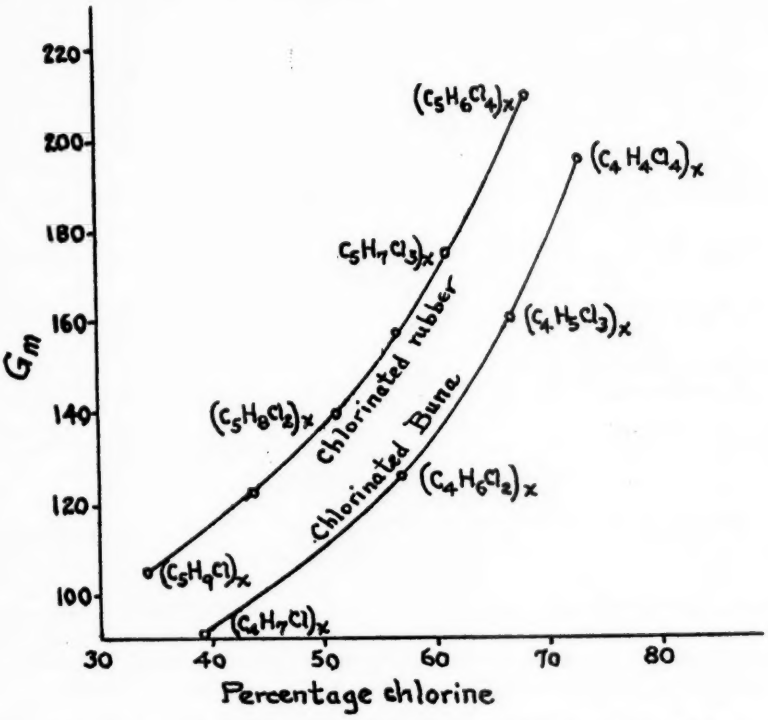


FIG. 5.—Curves for estimating the base molecular weights of chlorinated rubbers and of chlorinated Buna from their chlorine contents.

in every solvent tried, yet had the same chlorine content as that of the soluble product. Accordingly the formation of networks of insoluble products is particularly strong in Buna.

The technical grades of chlorinated rubbers, those prepared from sulfuryl chloride, and the different grades of chlorinated Buna contain very small percentages of oxygen. On the contrary, the chlorinated balata which was prepared with rigid exclusion of oxygen was completely free of oxygen, as shown by the analyses summarized in Table 12.

The base molecular weights of the chlorinated rubbers, chlorinated balatas and chlorinated Bunas were estimated by graphical extrapolation (see Figure 5).

K_m VALUES OF CHLORINATED RUBBER, CHLORINATED BALATA AND CHLORINATED BUNA

The molecular weights of the various products were estimated by osmotic measurements of toluene solutions, and by graphical extrapolation of the p/c values. The K_m values were estimated from the corresponding viscosity constants, as summarized in Table 13.

TABLE 13

K_m VALUES OF CHLORINATED RUBBER, CHLORINATED BALATA AND CHLORINATED BUNA

(Determined in toluene solutions)

Substance	Fraction	G_m	$\bar{M}$	$\bar{P}$	Z_η	$K_m \times 10^4$
Dartex	1	180	310,000	1700	0.065	0.38
	2	179	215,000	1200	0.046	0.38
	3	184	120,000	650	0.025	0.38
Tornesit (extra-high viscosity)	2	184	380,000	2100	0.073	0.35
Chlorinated rubber (prepared from SO_2Cl_2)	1	158	410,000	2600	0.077	0.30
Chlorinated balata	1	188	350,000	1850	0.057	0.31
	2	189	250,000	1300	0.041	0.32
Chlorinated balata (prepared from SO_2Cl_2)	2	150	190,000	1250	0.062	0.49
Chlorinated Buna-85 (laboratory preparation)	2	150	330,000	2200	0.065	0.30
	3	154	110,000	720	0.024	0.33
Chlorinated Buna-S (technical grade)	1	129	130,000	1000	0.035	0.35
	2	126	82,000	650	0.025	0.38

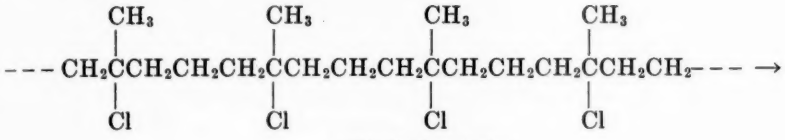
In spite of their high molecular weights, the chlorinated rubbers showed relatively low viscosities, and correspondingly very low K_m values, which are only about one-fifteenth the value of the K_m constant of squalene hydrochloride, determined experimentally.

CONSTITUTION OF CHLORINATED RUBBER

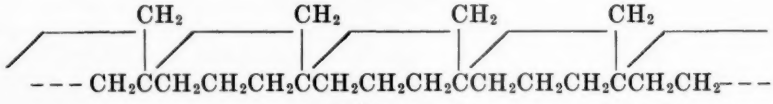
According to the experiments described in the preceding section, chlorinated rubbers have very high molecular weights. When transformed into highly chlorinated derivatives, rubber and balata are not degraded to any considerable extent, contrary to what had previously been assumed on the basis of the lower viscosities of solutions of chlorinated rubber. The surprisingly lower K_m values of chlorinated rubber are to be attributed rather to the fact that, in spite of the high molecular weights, molecules of chlorinated rubber are relatively short. Chlorinated rubbers, therefore, are probably not chlorine-substituted, high-molecular paraffinic derivatives, for if they were, their lower viscosity values would have to be explained on the assumption that their fibre molecules are kinked to a very high degree in solution, in accord with the views of Kuhn[1], whereas this assumption is untenable in the light of the experimental results of the study of polyprene hydrochlorides. The shortening of the molecules of

chlorinated rubber must, rather, be the result of still unknown cyclization reactions. From this point of view, chlorinated rubber represents a highly chlorinated cyclorubber, or, expressed otherwise, a highly chlorinated, branched, polycyclic polyterpene. In favor of this view is the experimental fact that chlorinated rubbers have small K_m values comparable to that of cyclorubber, the value[33] of which is 0.4×10^{-4}.

Since in the transformation of rubber into cyclorubber, the double bonds are to a great extent lost, it has heretofore been assumed that closing of the ring takes place, such as that which occurs, for example, in the transformation of geraniolene and cyclogeraniolene[50]. The formation of cyclorubber can be represented by the following scheme:



rubber hydrochloride



cyclorubber

If only this kind of cyclization reaction were to take place with a rubber hydrocarbon with unbranched fibre molecules of the constitution previously assumed, the chains would be shortened to only a slight extent in the transformation of rubber into cyclorubber or into chlorinated rubber. Actually, however, the shortening of the chains must be very considerable, for the K_m values of chlorinated rubbers and of cyclorubbers are only about one-fifth the K_m value of the original rubber. A shortening of the chains to such a great extent is, therefore, possible only if other unknown cyclization reactions take place. Such reactions are possible not only if the macromolecules of rubber and of Buna possess, as previously assumed, an unbranched fibrous structure, but also if they are assumed to have a branched structure, for in this case these side chains can react with the main chains through cyclization, with resulting marked shortening of the molecules.

It would be of particular interest to study the transformation of chlorinated rubbers into hydrocarbons by treatment with organometallic compounds, as in the case of rubber hydrochloride. The hydrocarbons should have very low viscosity constants for high molecular weights, *i.e.*, small K_m values like those of chlorinated rubber and cyclorubber. According to preliminary experiments, chlorinated rubbers react with lithium methyl and with lithium phenyl. It has not yet been possible, however, to investigate these transformation products any further[51]. It is worthy of note, however, that no success was obtained in making chlorinated rubber react with zinc ethyl, even after one month's contact. Its chlorine atoms are, therefore, united extraordinarily firmly, and are much less reactive than the chlorine atoms of polyvinyl chloride and of rubber hydrochloride, which are so much more easily attacked by this reagent.

This surprising degree of stability of chlorinated rubber is in contradiction to the previously suggested structure of a chlorine-substituted paraffin, for if this were so, it would be expected to be as reactive as rubber hydrochlorides

and polyvinyl chlorides. The comparative inactivity of the chlorine in chlorinated rubber is evidence in favor of the latter being a highly cyclized compound; for a similar lack of activity has been found with a low-molecular, highly chlorinated, cyclized terpene.

By chlorination of pinene hydrochlorides under extreme conditions, a chlorine derivative of unidentified constitution but of the empirical composition $C_{10}H_8Cl_{10}$ with a chlorine content of 72 per cent, has been obtained[52], and this, like chlorinated rubber, is extraordinarily stable. Also like chlorinated rubber, this chlorine derivative is not attacked by hot nitric acid, sulfuric acid, or aqueous alkalies, and even silver oxide does not split off chlorine by contact for as long as one month[52].

The view that chlorinated rubber is a highly chlorinated, polycyclic polyterpene explains, therefore, in the best way its physical and chemical properties, such as its surprisingly great resistance to various reagents, its ready solubility in most organic solvents, and its small K_m value. Because of these properties, it is easy to understand why chlorinated rubber has become particularly important technically, as, for example, in the manufacture of stable, durable varnishes, for in spite of its high molecular weight, it has a short chain length, and therefore highly concentrated solutions can be prepared. The size and the form of the molecule are probably responsible for the fact that films of chlorinated rubber have good adhesive properties. Since the chlorination and cyclization of rubber follow very different courses, it is to be expected that the macromolecules of chlorinated rubber have a very characteristic structure, *e.g.*, chlorinated rubber has no tendency to crystallize, and consequently films of chlorinated rubber show none of the aging phenomena which result from crystallization.

THE K_m VALUES AND THE FORM OF MACROMOLECULES

Among the various types of rubbers and their halogen derivatives, numerous cases are to be found where substances with approximately the same mean degrees of polymerization have widely different viscosity constants, and therefore widely different K_m values as well, as may be seen in Table 14.

If it is assumed, as has been done by Ostwald[55], that the viscous properties of colloidal solutions differ fundamentally from those of low-molecular solu-

TABLE 14

Z_η VALUES OF RUBBER HYDROCARBONS AND THEIR DERIVATIVES OF APPROXIMATELY THE SAME DEGREES OF POLYMERIZATION IN TOLUENE

Substance and its fraction	$\bar{P}$	$K_m \times 10^4$	Z_η
Emulsion polymer (prepared with much control agent)[35]; middle fraction	1400	1.6	0.220
Chloroprene	1300	1.65	0.214
Gutta-percha II[53]	1550	1.4	0.210
Balata II[53]	1450	1.3	0.188
Hydrochlororubber IV[2]	1450	1.3	0.187
Hydrogutta-percha[53]	1100	1.2	0.130
Evonymus gutta-percha II[54]	1350	1.1	0.143
Buna-85 (easily soluble fraction)[35]	1450	1.0	0.144
Masticated rubber (easily soluble fraction)[53]	1350	0.81	0.110
Ethylhydrobalata I	1200	0.72	0.087
Hydrochlorobalata I 1	1400	0.67	0.094
Hydrochlorobalata II 2	1400	0.63	0.088
Dartex 2	1200	0.38	0.046
Chlorinated balata 2	1300	0.32	0.041

tions in that, in the case of colloidal solutions, these properties depend on a large number of factors, *e.g.*, the degree of dispersion, solvation, ionization, thermal and mechanical pretreatment, aging, etc., whereas the viscous properties of low-molecular solutions in any given solvent depend only on the temperature and concentration, then differences in the viscosity constants of colloidal substances with the same degrees of polymerization should be considered as of little significance, because it is impossible to decide which of the various factors are to be held responsible for the differences in their viscosity constants.

An entirely different view must be taken if the viscosities of these macromolecular substances are considered on the same basis as low-molecular compounds[56]. In this case, the viscosity constant of the dissolved substance has a characteristic value which depends on the form and solvation of the molecules. The K_m values, the proportionality factors between the molecular weights and viscosity constants, therefore, give in this case a valuable means of insight into differences in the form of the molecules; for differences in solvation can be disregarded in comparing the K_m values of high-polymer hydrocarbons of different structures, since it may be assumed that they are equally solvated in good solvents. If, on the other hand, the K_m values of hydrocarbons and their halogen derivatives are the subject of comparison, it would be expected that the halogen derivatives, with the same form of molecules, would have higher K_m values than those of the corresponding hydrocarbons, perhaps because of better solvation of their molecules, as is true of squalene hexahydrochloride. Actually all halogen derivatives have lower K_m values, and chlorinated rubbers much lower K_m values, than those of the corresponding hydrocarbons, and therefore these differences must be attributed, not to differences in solvation, but solely to differences in molecular form. Consequently in the case of rubber derivatives it must be assumed that the smaller the K_m values, the more highly cyclized are the compounds. In other words, compounds with the highest K_m values have the most elongated, or the least branched and least cyclized molecules, whereas the macromolecules of chlorinated rubber and of cyclorubber have relatively short chains and are highly cyclized. Changes in length of the molecules, which are manifest by the K_m values, are manifest in great changes in physical properties of a substance. On the basis of the experiments described in the present work, it can be concluded, for example, that, with increasing degree of cyclization, *i.e.*, with shortening of the molecules, the elastic properties of rubber become less pronounced.

INCREASE IN THE η_{sp}/c VALUES AT HIGHER CONCENTRATIONS

The η_{sp}/c values of unbranched macromolecular compounds do not remain constant with increase in concentration, but show appreciable increases even at low concentrations of the solutions; and the higher the viscosity constant, in other words, the greater the chain length of the compound, the greater is this increase. This increase in η_{sp}/c value with increase in concentration is attributable to destruction of the long fibre molecules, whose sphere of action is not directly proportional to the chain length, but to the square of the chain length[57]. This increase in η_{sp}/c value does not depend on the molecular weight, but only on the viscosity constant, *i.e.*, on the chain length of the elongated molecules.

Among different types of rubber, numerous examples are to be found which prove that substances with approximately the same average degrees of polymerization show different increases in their η_{sp}/c values; in fact, the increases

are those which would be expected of substances with elongated molecules, *i.e.*, substances with high K_m values show much greater increases than do substances with low K_m values, *i.e.*, those with relatively short molecules. Cases are even found where substances of higher degrees of polymerization show much smaller increases in viscosity than do substances of lower degrees of polymerization when the former have lower viscosity constants than the latter. This is evident from the data in Table 15 and from Figure 6.

TABLE 15

INCREASES IN THE η_{sp}/c VALUES OF RUBBER DERIVATIVES AT HIGH CONCENTRATIONS IN TOLUENE

Substance	$\bar{P}$	$K_m \times 10^4$	Z_η	c (g. per l.)	η_r	η_{sp}/c
Chloroprene	1300	1.65	0.214	0.52	1.112	0.214
				2.00	1.470	0.235
				4.00	2.100	0.275
				6.00	2.990	0.332
				8.00	3.980	0.372
				10.00	5.280	0.428
Hydrorubber[58] (in cyclohexane)	1250	1.4	0.174	1.45	1.252	0.174
				5.00	2.014	0.203
				10.13	3.652	0.261
				15.02	5.856	0.324
Ethylhydrorubber (III)	1900	0.95	0.180	1.26	1.226	0.179
				4.68	2.049	0.224
				9.88	3.986	0.302
Hydrochlorobalata (I 1)	1400	0.67	0.094	2.07	1.195	0.094
				5.33	1.542	0.102
				7.61	1.840	0.110
				12.32	2.538	0.125
Ethylhydrobalata (I)	1200	0.72	0.087	1.72	1.150	0.087
				2.36	1.204	0.087
				4.92	1.451	0.092
				10.34	2.136	0.110
Chlorinated rubber (by SO_2Cl_2)	2600	0.30	0.077	1.31	1.109	0.077
				2.77	1.219	0.079
				6.10	1.518	0.085
				12.07	2.161	0.096
Chlorinated Buna-85 (2)	2200	0.30	0.065	1.64	1.106	0.065
				2.58	1.167	0.065
				5.54	1.381	0.069
				10.04	1.770	0.077
				15.50	2.353	0.087

THE RELATIONS BETWEEN ELASTICITY, MOLECULAR SIZE AND MOLECULAR FORM

It is only necessary to compare the physical properties of macromolecular substances to be aware that rubberlike elasticity exists only when the substances have straight-chain structures[59]. Elasticity is, therefore, not only closely related to molecular form but, in addition, the elongated molecules must have a minimum length; for insofar as rubber, hydrorubber[60], and poly-

isobutylenes[61] are concerned, it has been found that only those products with the highest molecular weights, *i.e.*, eucolloid members, are outstandingly elastic, whereas degraded, hemicolloid products are sticky, viscid substances. All these facts can be reconciled with the concept of Kuhn, according to which the coiled fibre molecules are stretched out during elastic extension. However, as already mentioned, other observed facts, such as the validity of the viscosity law, point to fibre molecules having stable forms. Furthermore, the observations described in the present work cannot be reconciled with the concepts of Kuhn. If the molecules do have stable forms, then elasticity cannot be explained by a stretching out of the fibre molecules, whereas it is possible to explain it by a gathering together of small bundles of molecules into larger bundles. The crystallization phenomena which become manifest when rubber

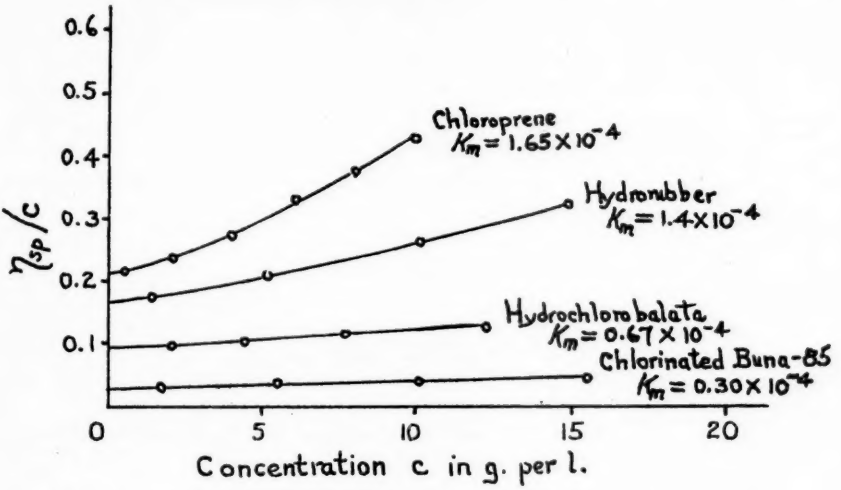


FIG. 6.—Increase in the η_{sp}/c values of rubber derivatives with increase in concentration.

is stretched can perhaps be explained by assuming first of all that the bundles of molecules in their original, unstretched state have such small dimensions that they cannot be detected by roentgenographic methods. During stretching, these subroentgenographic bundles of molecules assemble into larger bundles, which can be detected roentgenographically. In this process, softening agents promote slipping of the bundles of molecules[62].

Finally it will be possible to explain the relation between elasticity and constitution only when the constitution of rubber, which is the outstandingly characteristic member among rubberlike substances[63], becomes known. The extraordinarily high elasticity of rubber may also be an indication that the side chains of its branched macromolecules function as internal softening agents. During elastic stretching, the valence angles of these side chains are perhaps deformed; forces of elasticity would then be set up as a result of the transformation of bundles of macromolecules with deformed side chains back into bundles of macromolecules of the original form or structure. On this basis, the side chains in rubber would be responsible for its particularly high elasticity. It would be understandable also why the elastic properties of Buna are characteristically different from those of rubber, for the character of the

branching and the side chains in the macromolecules of Buna are unquestionably different from those in rubber[35].

The concept already expressed[59] that the elasticity exhibited by many high-polymer substances is manifest only within limited ranges of temperature should, therefore, be modified by adding that the macromolecules must also have a particular characteristic structure. To prove conclusively this working hypothesis, the elasticity of substances of similar structures, on the one hand with fibre molecules, and on the other with branched molecules, must be investigated. In addition to this, an investigation should be made as to what extent the elasticity or the plasticity of substances composed of fibre molecules is increased by softening agents; for plasticity depends to a much less extent on a special molecular structure than does rubberlike elasticity.

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[19] Harries has described an impure product of this composition, and states that the chlorine content is lowered by reprecipitation (cf. Harries, "Natürliche und künstliche Kautschukarten", Berlin, Verlag Springer, **1919**, p. 17).
[20] For the balata latex we are grateful to the Norddeutsche Seekabelwerke Nordenham; the rubber latex was furnished by O. Schweitzer, to whom we wish to show our appreciation.
[21] The solutions were freed of atmospheric oxygen by distillation in pure carbon dioxide.
[22] According to Harries ("Natürliche und künstliche Kautschukarten", Berlin, Verlag Springer, **1919**, p. 21), the hydrohalides are transformed back into the hydrocarbons by organic bases. Isorubber prepared in this way is, however, a highly cyclized product.
[23] With regard to the cyclization of rubber hydrochlorides, see Staudinger and Widmer, *Helv. Chim. Acta* **9**, 529 (1926).
[24] All microanalyses were made by S. Kautz.
[25] All products were ash-free.
[26] The mean molecular weight, $\overline{M}$, and the mean degree of polymerization, $\overline{P}$, were obtained by osmotic measurements or by determining the end groups. The values obtained by viscometric measurements are designated as the average molecular weights DM or average degrees of polymerization DP (cf. Staudinger, "Organische Kolloidchemie", Verlag Vieweg, 2nd Ed., **1941**, p. 93).
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MOLECULAR WEIGHTS OF HIGH POLYMERS *

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The molecular weights of small molecules can readily be determined, either from measurements of certain of their properties in the gaseous state or from measurements of certain properties (osmotic pressure, freezing point depression, etc.) of their dilute solutions. The molecular weights of very large molecules, however, cannot be determined from gaseous state data because of their very low vapor pressures. Moreover, the application of the usual equations relating osmotic pressure and similar properties of a solution to the determination of molecular weights of very large solute molecules leads, in general, to large errors. These equations are, theoretically and experimentally, truly applicable only to infinitely dilute solutions. If they are incorrectly used

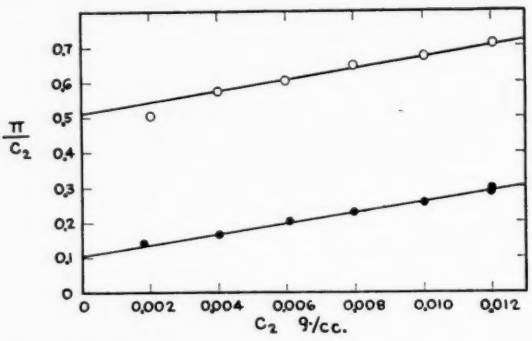

FIG. 1.—Dependence of osmotic pressure on concentration for solutions of two fractions of chlorinated polyvinyl chloride (per cent Cl ≈ 66) in dioxane at 27° C. Data by Staudinger and Schneiders[5]; $\mu_1 = 0.38$.

for solutions of finite concentration, an error is introduced, both for small-molecule and for large-molecule solutes. Comparing measurements for two solutes which are similar except for their size in the same solvent and at the same concentration and temperature, the magnitude of the error in the calculated reciprocal of the molecular weight ($1/M_2$) is about the same in the two cases. This leads to a much greater error in the molecular weight in the case of a macromolecular solute than in the case of a small-molecule solute. This may be illustrated by Figure 1, which shows the relation between osmotic pressure (Π, in atmospheres) and concentration (C_2, in grams of solute per cc. of solution), for solutions in dioxane of two fractions of chlorinated polyvinyl chloride.

The equation:

$$\frac{\Pi}{C_2} = \frac{RT}{M_2} \tag{1}$$

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where R = gas constant, cc. atm./degree mole
T = absolute temperature
is thermodynamically correct at infinite dilution. Extrapolation of the experimental data, plotted in Figure 1, to infinite dilution ($C_2 = 0$) gives intercepts indicating, according to Equation 1, molecular weights of 48,000 and 242,000 for the two fractions. If, however, one (incorrectly) substitutes the observed Π/C_2 values into Equation 1, "molecular weights" ranging from 35,000 to 49,000 for one sample and from 82,000 to 172,000 for the other are deduced. The error resulting from the use of Equation 1 for solutions of finite concentration (in the usual experimental range) is thus far from negligible, and is greater, the larger the molecular weight (other things being equal).

The difficulty is aggravated by the fact that accurately measurable values of the osmotic pressure of high polymer solutions are not readily obtained in very dilute solutions.

Although still neglected by some workers[1], these facts have been recognized by others[2]. It has been found empirically that graphs of Π/C_2 (or ϑ/C_2, if the data are measurements of freezing point depressions, ϑ) against C_2 show an approximately rectilinear relation (Figure 1). Such graphs are useful, therefore, in extrapolating to $C_2 = 0$ to obtain limiting values of Π/C_2 (or ϑ/C_2) which can properly be substituted into Equation 1 (or into the corresponding equation relating the freezing point depression to the molecular weight).

A theoretical explanation for the approximate rectilinear relation between Π/C_2 (or ϑ/C_2) and C_2 was furnished by the statistical treatment of the thermodynamic properties of long-chain molecules, developed independently by Flory[3] and the writer[4]. This theoretical treatment also explains the different slopes of the lines obtained for different systems in terms of molecular properties and accounts for the deviations from the straight-line relation which occur at higher concentrations.

The new theoretical equation, for the osmotic pressure case, may be written:

$$\frac{\Pi}{C_2} - \frac{RTd_1C_2^2}{3M_1d_2^3} - \cdots = \frac{RT}{M_2} + \frac{RTd_1}{M_1d_2^2}\left(\frac{1}{2} - \mu_1\right)C_2 \qquad (2)$$

where d_1, d_2 = densities of solvent and solute, respectively
M_1, M_2 = molecular weights of solvent and solute, respectively
μ_1 = a constant depending on nature of solvent and solute, but not on molecular weight of the latter

The second term on the left in Equation 2 is negligible for many osmotic pressure studies. This is also true of the terms involving higher powers of C_2, represented in the equation by dots. Inclusion of this second term would lower the points at highest C_2 values (Figure 1) only about 0.004, approximately the width of the straight lines in the graph.

Flory's recent study[6] of osmotic pressures of solutions of polyisobutylene in cyclohexane may be cited as an example of an instance in which the second term of Equation 2 is not negligible. (Contrary to Flory's statements in this paper, his experimental results are in entire agreement with the theoretical conclusions published by the writer.) As Figure 2 shows, much of the curvature obtained when the ratio of osmotic pressure to concentration is plotted against concentration is removed when the additional term is included. (The remaining curvature, if real, can be attributed to a slight dependence of μ_1 on concentration, a change from $\mu_1 \approx 0.42$ at $c = 0$, to $\mu_1 \approx 0.41$ at $c = 2$ grams per 100 cc.)

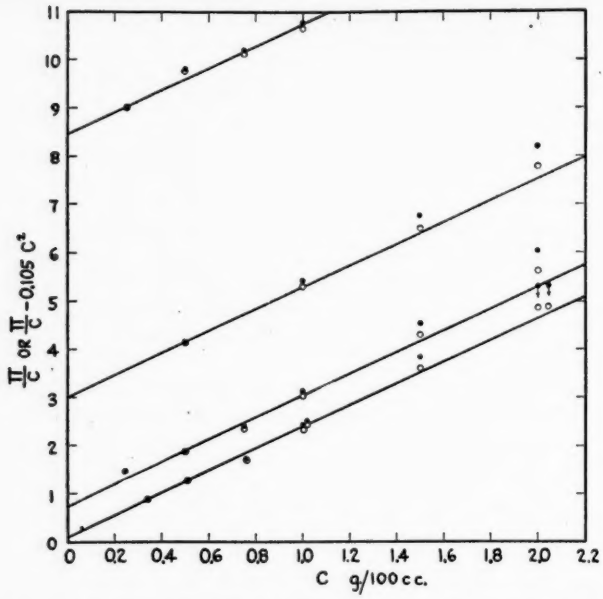

FIG. 2.—Dependence of osmotic pressure on concentration for solutions of polyisobutylene in cyclohexane at 25° C. Data by Flory[6]. The ordinates are Π/c for the filled circles, $\frac{\Pi}{c} - \frac{RTd_1c^2}{3M_1d_2^3}$ for the open circles; Π is in grams/sq. cm.; c is in grams/100 cc. of solution.

An alternative method of plotting osmotic pressure, cryoscopic, or other similar data is shown in Figures 3, 4, and 5. This method is based on the theoretical Equation[7]:

$$\phi \equiv \frac{\ln a_1 - \ln V_1}{V_2} - 1 = -\frac{\bar{V}_1}{V_2} + \mu_1 V_2 \qquad (3)$$

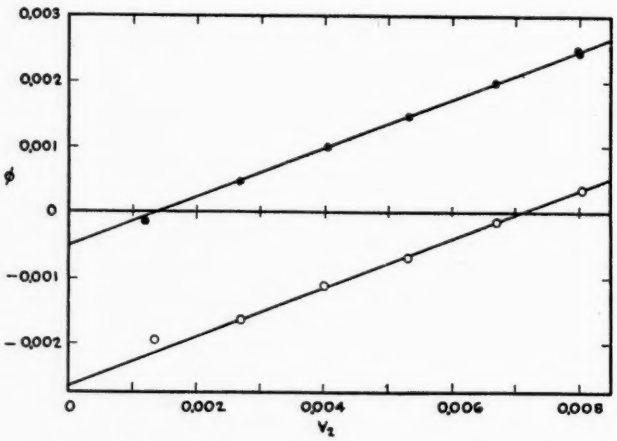

FIG. 3.—Alternative method of showing dependence of osmotic pressure on concentration (equation 3). Same data as for Fig. 1; $\mu_1 = 0.38$.

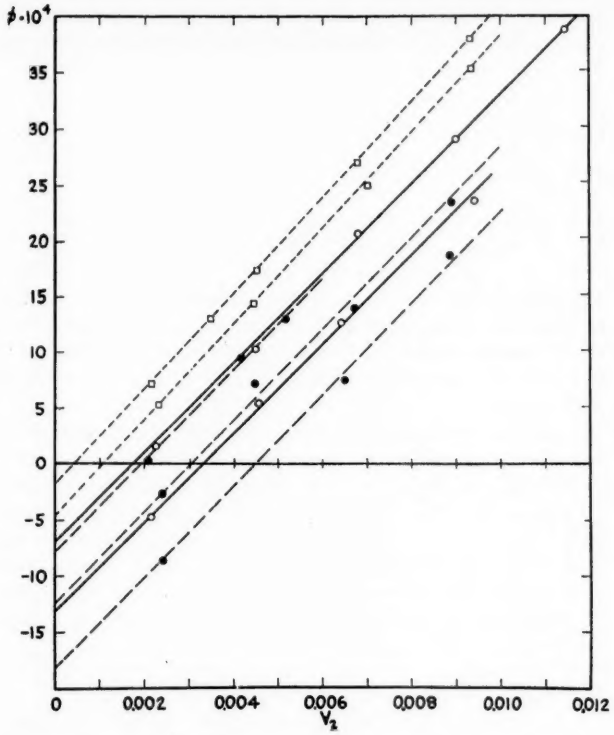

FIG. 4.—Dependence of osmotic pressure on concentration for solutions of polybutadiene fractions in toluene at 27° C. Data by Staudinger and Fischer[9]:

——— ○ Sodium polymer, B85.
— — ● Emulsion polymer, polymerized with much controlling agent.
- - - - □ Emulsion polymer, polymerized with little controlling agent.

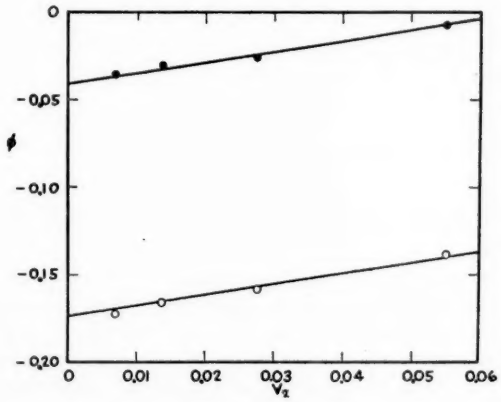

FIG. 5.—Dependence of activity function ϕ (equation 3) on volume fraction for polystyrene solutions in cyclohexane. Cryoscopic data by Kemp and Peters[12]; $\mu_1 = 0.62$.

where A_1, A_2 = volume fractions of components
$\overline{V}_1$, $\overline{V}_2$ = partial molal volumes of components
$\overline{V}_1 \approx V_1 = M_1/d_1$ (4)
$\overline{V}_2 \approx V_2 = M_2/d_2$ (5)
and a_1 = activity of solvent

a_1 is related to the osmotic pressure by the equation:

$$\ln a_1 = -\frac{\Pi \overline{V}_1}{RT} \tag{6}$$

and to the freezing point lowering by a similar equation. Plotting ϕ against V_2, the experimental points for a given polymer sample obey a straight-line relation within the probable experimental error. The intercept of this straight line with the ordinate axis gives $-\overline{V}_1/\overline{V}_2$, from which, by Equations 4 and 5, M_2 can be computed.

This method of plotting has the advantage of being applicable to relatively high concentrations (provided μ_1 remains constant) without the introduction of additional terms. It also gives the constant μ_1 directly, as the slope of the straight line obtained. Once μ_1 is known for a given polymer-solvent combination, a single good osmotic pressure or cryoscopic measurement suffices to determine the molecular weight of the solute. (Of course one must not assume the same value of μ_1 for two copolymers consisting of the same monomeric units but in different proportions, or for two polymers which are otherwise chemically different.) The apparent slight variation of μ_1 with average molecular weight (Figure 6) for polymethyl methacrylate fractions in acetone is

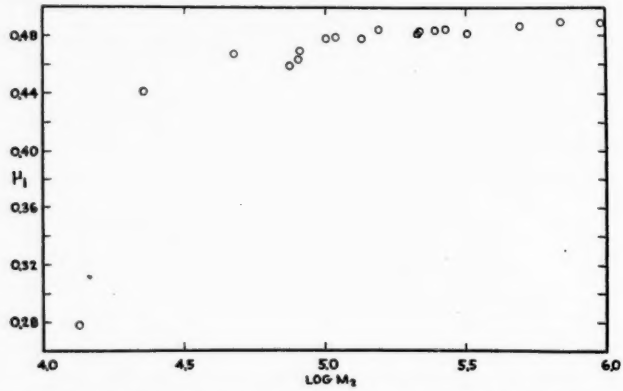

FIG. 6.—Apparent variation of μ_1 with number-average molecular weight, for polymethylmethacrylate fractions in acetone at 27° C. Osmotic pressure data by Schulz and Dinglinger[15].

probably the result of slight chemical differences between the average molecules of the different fractions or of the presence of small amounts of impurities, rather than a true dependence on the molecular weight of the polymer.

Samples of high polymers, as normally obtained, are always mixtures of chains of different length and, hence, of different molecular weight. The molecular weights obtained from osmotic or cryoscopic data by either of the procedures just outlined are averages; these are ordinary number averages,

defined as the total weight of the molecules (in molecular weight units) divided by the number of molecules (N):

$$ {}_n\bar{M} = \frac{\sum_{i=1,2\ldots}^{N} M_i}{N} \tag{7} $$

A small percentage (by weight) of small molecules (or ions) in a high polymer has a large effect on the number-average molecular weight. For instance, 1 per cent of a compound of molecular weight 100 in a polymer of molecular weight 100,000 reduces the average molecular weight to about 10,000. Great care should therefore be exercised in interpreting average molecular weights, obtained from osmotic or cryoscopic data on high polymeric materials which may also contain molecules of low molecular weight.

Much use has been made of a relation[8] known as Staudinger's law or Staudinger's rule, an assumed proportionality between the ratio of specific viscosity (η_{sp}) to concentration (in any of various units) and the average molecular weight:

$$ \left(\frac{\eta_{sp}}{c}\right)_c = K\bar{M} \tag{8} $$

The specific viscosity is defined by the equation:

$$ \eta_{sp} \equiv \frac{\eta}{\eta_0} - 1 \tag{9} $$

where η = viscosity of solution
η_0 = viscosity of pure solvent

Considerable evidence has accumulated showing that, although Equation 8 is approximately correct (especially if a small empirical constant is added) for certain systems over large ranges of molecular weight, it is not of general validity, whether the ratio η_{sp}/c is measured at a fixed finite value of the concentration or is the extrapolated value at infinite dilution (Figures 7 to 12).

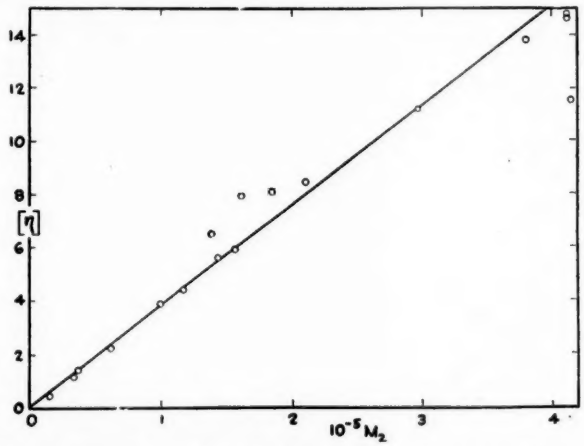

FIG. 7.—Dependence of intrinsic viscosity on molecular weight for cellulose nitrate fractions in acetone at 27° C. Osmotic pressure data by Husemann and Schulz[16]; $[\eta] = 3.8 \times 10^{-5} M_2$.

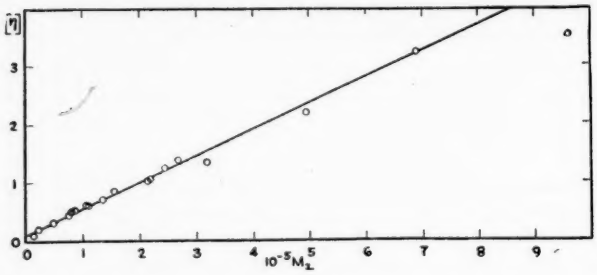

FIG. 8.—Dependence of intrinsic viscosity on molecular weight for polymethylmethacrylate fractions in chloroform at 20° C. Data by Schulz and Dinglinger[15]; $[\eta] = 0.1 + 4.5 \times 10^{-6} M_2$.

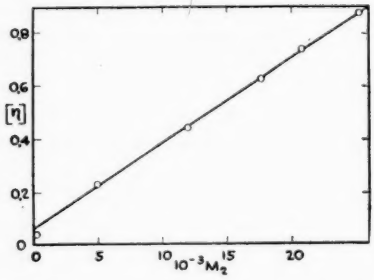

FIG. 9.—Dependence of intrinsic viscosity on molecular weight for ω-hydroxyundecanoic self-polyesters in chloroform at 25° C. Data by Baker, Fuller, and Heiss, Jr.[20]; $[\eta] = 0.06 + 3.2 \times 10^{-5} M_2$.

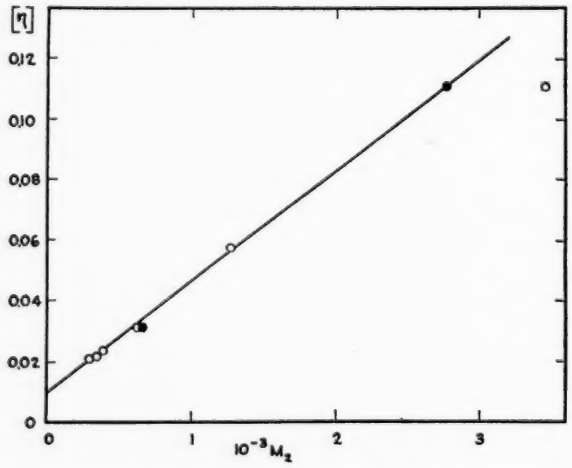

FIG. 10.—Dependence of intrinsic viscosity on molecular weight for polystyrene fractions in benzene (at 25° C?). Data by Kemp and Peters[13]; $[\eta] = 0.01 + 3.55 \times 10^{-5} M_2$.

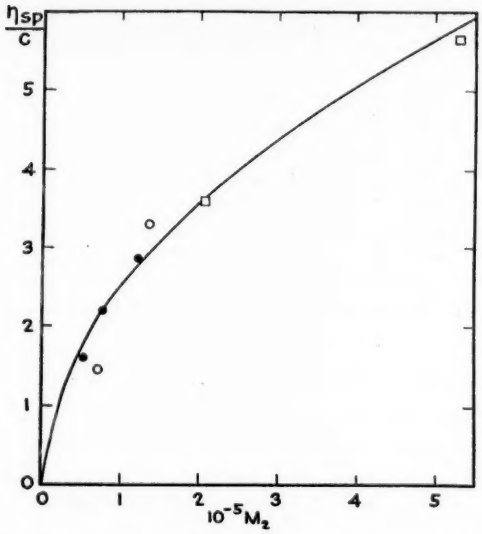

FIG. 11.—Dependence of η_{sp}/c (measured at c values between 0.04 and 0.1 gram/100 cc.) on the number-average molecular weight for solutions of butadiene polymer fractions in toluene at 20° C. The curve corresponds to Equation 17, with $k = 0.008$ and $\nu = 0.5$, and assuming M to equal the number-average molecular weight. Data by Staudinger and Fischer[9]. The polymers are distinguished in the same manner as in Fig. 4.

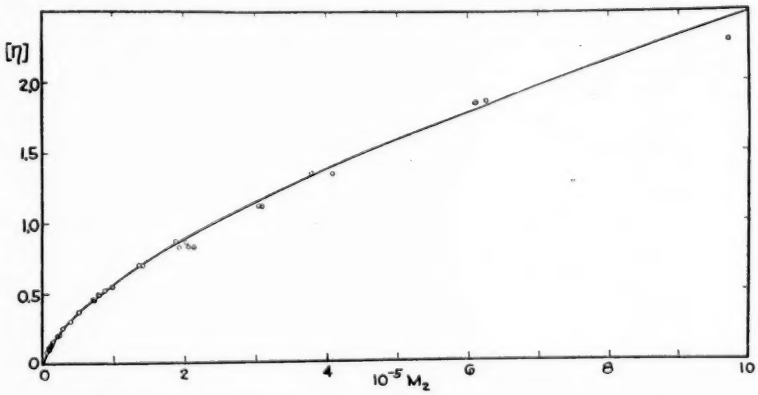

FIG. 12.—Dependence of intrinsic viscosity on molecular weight for polyisobutylene fractions in diisobutylene at 20° C. Data by Flory[6]; $[\eta] = 3.60 \times 10^{-4} M_2^{0.64}$. (Two experimental points, for $M_2 > 10^6$, are omitted.)

This limiting value of the ratio (for c in grams per 100 cc. of solution) was defined by Kraemer[10] as the intrinsic viscosity, represented by $[\eta]$:

$$[\eta] \equiv \left(\frac{\eta_{sp}}{c}\right)_{c=0} \equiv \left(\frac{\ln (\eta/\eta_0)}{c}\right)_{c=0} \tag{10}$$

It has been shown theoretically[11], moreover, that Equation 8 should not be generally valid. Plots of $[\eta]$ against $\bar{M}$, or of $(\eta_{sp}/c)_c$ against $\bar{M}$, should and do deviate from rectilinearity, often markedly; the deviations depend,

according to the theory, on tightness or looseness of coiling of the kinked double-chain molecules and on other factors. Measurements of the viscosity of solutions of polymers can validly be used to estimate molecular weights only if the course of the (intrinsic) viscosity *vs.* molecular weight curve is known.

It may be noted in passing that deviations from Staudinger's rule furnish no justification for assuming that the polymer chains are branched[12]. It is equally reasonable to assume that these deviations result from variations in the compactness of kinking of unbranched chain molecules; such an assumption is in better agreement (in certain cases, at least) with other facts, such as the differences in the viscosity-molecular weight relation in different solvents. Doubtless the chains are branched in some materials of high molecular weight, but deviations from Staudinger's rule cannot justifiably be cited as pertinent evidence.

The use of $[\eta]$, rather than $(\eta_{sp}/c)_c$ or $\left(\frac{\ln(\eta/\eta_0)}{c}\right)_c$ at some arbitrary concentration other than zero, is to be recommended, both because of the simpler theoretical interpretation and for convenience in comparing viscosity data obtained at different concentrations. From measurements at finite concentrations, $[\eta]$ is easily obtained by means of the relation[14]:

$$\frac{\eta_{sp}}{c} = [\eta] + k'[\eta]\eta_{sp} \tag{11}$$

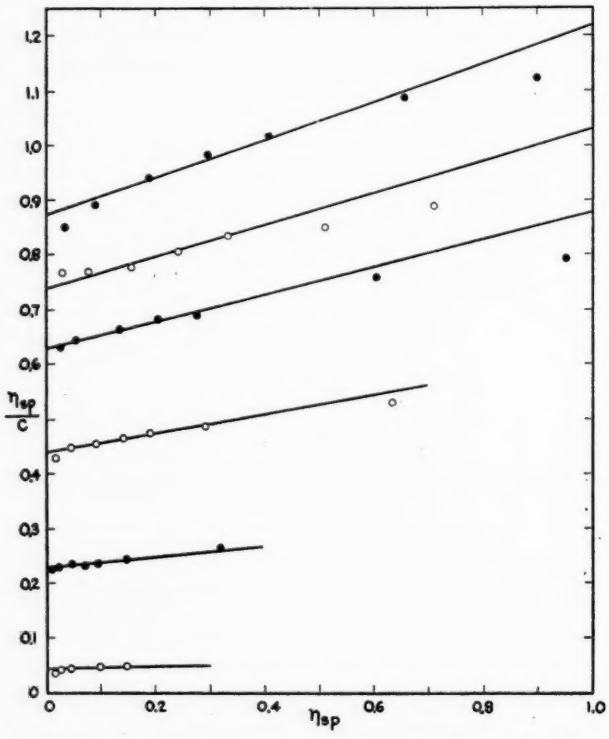

FIG. 13.—Dependence of viscosity on concentration (equation 11) for solutions of ω-hydroxyundecanoic self-polyesters in chloroform at 25° C. Data by Baker, Fuller, and Heiss[20]; $k' = 0.395$.

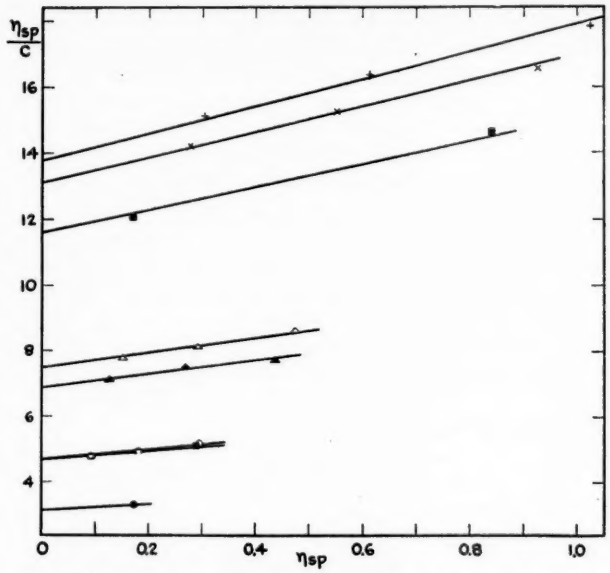

FIG. 14.—Dependence of viscosity on concentration for solutions of polyvinyl chloride in cyclohexanone at 25° C. Data by Mead and Fuoss[22]; $k' = 0.32$.

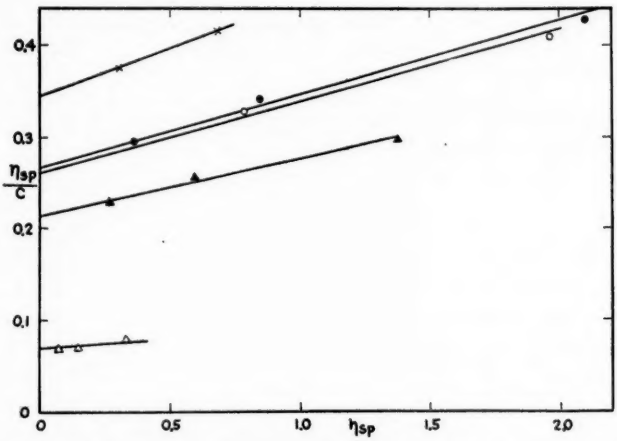

FIG. 15.—Dependence of viscosity on concentration for solutions of rubber fractions in cyclohexane at 25° C. Data by Kemp and Peters[23]; $k' = 0.30$.

which may also be written:

$$[\eta] = \frac{\frac{\eta_{sp}}{c}}{1 + k'\eta_{sp}} \tag{12}$$

Like μ_1, k' depends on the type of polymer, on the solvent, and on the temperature, but only slightly or not at all on the molecular weight of the polymer.

This relation has a sound theoretical basis, and has been amply verified experimentally (Figures 13 to 15). The value of k' for a given polymer-

solvent combination can be deduced from a series of measurements on a polymer sample at different concentrations. For this purpose the polymer need not be homogeneous as regards molecular weight. A convenient procedure is to plot η_{sp}/c against η_{sp} and to draw the best straight line through the experimental points. The ratio of the slope to the intercept (at $c = 0$) is k'. Once this constant has been determined, a single viscosity measurement suffices to determine $[\eta]$ and, hence, the molecular weight if the $[\eta]$ *vs.* M curve is also known. Alternatively, one may plot η_{sp}/c or $\frac{\ln(\eta/\eta_0)}{c}$ against c. The limiting slope, assuming Equation 11 to hold, is then $k'[\eta]^2$ or $(k' - \frac{1}{2})[\eta]^2$.

A "molecular weight" obtained in this manner for a polymer sample consisting of a mixture of molecules of various sizes is not the ordinary number average[17]. This becomes obvious on consideration of the following approximate theoretical equations[11] for the viscosities of dilute solutions of long-chain molecules.

For rodlike chain molecules,

$$[\eta] \approx K_2 \frac{\sum M}{\sum M_i} \tag{13}$$

For randomly kinked chain molecules,

$$[\eta] \approx K_1 \frac{\sum M_i^2}{\sum M_i} \tag{14}$$

For comparison, Einstein's theoretical equation[18] for large spherical molecules may be written:

$$[\eta] \approx K_0 = K_0 \frac{\sum M_i}{\sum M_i} \tag{15}$$

One may guess that, for solutions of actual chain polymers, the following more general relation will be found to hold:

$$[\eta] \approx K \frac{\sum M_i^{\nu+1}}{\sum M_i} \tag{16}$$

where ν denotes a number, not necessarily integral, between 0 and 2, its value depending on the nature of the solute and solvent molecules and on the temperature. Usually, ν should be less than one.

For molecularly homogeneous samples, Equation 16 reduces to

$$[\eta] \approx KM^{\nu} \tag{17}$$

This form of equation has been proposed by various authors, probably first by Mark[19].

There are few satisfactory data in the literature, on sufficiently well-fractionated polymer samples of accurately determined molecular weight, for testing the accuracy of this relation. Such data as are available, however, suggest its approximate validity. For example, Figure 11 shows the dependence of the ratio η_{sp}/c on the number-average molecular weight (determined by extrapolation of osmotic pressure data to infinite dilution; see Figure 4) for solutions of fractions of polybutadiene in toluene, according to data published by Staudinger and Fischer[9]. The viscosity data are insufficient to show the dependence of η_{sp}/c on concentration; hence, extrapolation to infinite dilution is impossible. This affects the dependence on molecular weight only

slightly, however; much more important is the fact that the fractions used for the viscosity measurements were far from homogeneous, as regards molecular weight. Similar results, obtained by Flory[6] from solutions of polyisobutylene fractions of greater probable homogeneity, are shown in Figure 12.

If a relation (graphical or analytical)

$$[\eta] = f(M) \tag{18}$$

between intrinsic viscosity and molecular weight is determined empirically from viscosity measurements on solutions of polymers which are essentially molecularly homogeneous, the application of this relation to solutions of polymers which are mixtures of molecules of different sizes gives an average molecular weight which differs from the number average, defined by Equation 7. If Equation 16 is obeyed, this new average is

$${}^{\nu}\bar{M} = \left(\frac{\sum M_i^{\nu+1}}{\sum M_i}\right)^{1/\nu} \tag{19}$$

which reduces to

$${}^{w}\bar{M} = \frac{\sum M_i^2}{\sum M_i} \tag{20}$$

the equation for the weight average of Kraemer and Lansing[21], if Staudinger's rule is obeyed; *i.e.*, if $\nu = 1$.

Flory[6] suggested that the average molecular weight obtained from properly interpreted viscosity measurements be termed a "viscosity-average" molecular weight. This is insufficient identification, however, since the equation defining the type of average depends on the nature of both solvent and solute and on the temperature, as well as on the fact that it is deduced from viscosity data. For "the average molecular weight" to have a definite meaning, it is probably necessary to specify that it is "the viscosity-average for a certain type of polymer in a certain solvent at a certain temperature". If it should prove true that Equation 16 is a good approximation, this designation can be simplified to "the average for ν equal to a certain value".

The largest molecules in a polymer mixture are relatively more important and the smallest molecules relatively less important in determining any of the viscosity averages than in determining the number average. A viscosity-average molecular weight is thus more appropriate than a number-average molecular weight for correlation with other properties which depend primarily on the presence and size of very large molecules, and which are only incidentally affected by the presence of small amounts of much smaller molecules.

SUMMARY

1. The equations generally used for the calculation of molecular weights from osmotic pressure or cryoscopic data are valid only at infinite dilution; their use with data obtained at finite concentrations (without extrapolation to infinite dilution) leads to very large errors, if the solute molecules are large.

2. In extrapolating osmotic or cryoscopic data to infinite dilution, graphs of Π/c (or ϑ/c) against c are useful and show a rectilinear relationship. At concentrations which are not very low, a correction term should be subtracted, or the quantity $\ln a_1 - \ln V_1/V_2) - 1$ should be plotted against V_2. For both types of graph the slope is characteristic of the solute-solvent system and the temperature, but is independent of molecular weight.

3. The use of Staudinger's rule to obtain molecular weights of high polymers is, theoretically and experimentally, unjustifiable, for most polymer-solvent systems at least. The more general relationship,

$$[\eta] \equiv \left(\frac{\eta_{sp}}{c}\right)_{c=0} = KM^{\nu}$$

where K and ν are constants to be determined empirically, is certainly more satisfactory, but whether or not this form of equation is really adequate remains to be proved. At present, empirical $[\eta]$ *vs.* M curves must be determined, using polymer samples which are molecularly homogeneous, before true molecular weights can be deduced from viscosity data.

4. Theoretically and experimentally it is preferable to relate the molecular weight to $[\eta]$, rather than to η_{sp}/c or $\ln(\eta/\eta_0)/c$ at some finite concentration. Extrapolation to infinite dilution is readily accomplished by means of graph of η_{sp}/c *vs.* η_{sp}. The ratio of the slope of the straight line obtained to its intercept depends on the type of solute and solvent and on the temperature but not on the molecular weight of the solute.

5. Osmotic pressure and cryoscopic measurements yield ordinary number-average molecular weights. Viscosity data, properly interpreted, yield another sort of average, in which the heavier molecules are relatively more important. The exact nature of this average depends on the $[\eta]$ *vs.* M curve (or on the value of ν in the equation $[\eta] = KM^{\nu}$).

6. If, for a given type of polymer, one knows (1) the constant (μ_1) determining the dependence of the osmotic pressure (in a suitable solvent) on concentration, (2) the constant (k') determining the dependence of the viscosity (in a suitable solvent) on concentration, and (3) the constants (K and ν) determining the dependence of the intrinsic viscosity on molecular weight (or an empirical curve showing this dependence); than a single osmotic pressure measurement and a single viscosity measurement on a given sample suffice to give the number-average molecular weight and a viscosity-average molecular weight (the meaning of which depends on the magnitude of ν). These two together give a better characterization of the polymer sample than either alone.

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TRANSPARENCY OF RUBBER AND ITS SOLUTIONS *

HENRY P. STEVENS

When rubber is dissolved in benzene or a mixture of coal-tar hydrocarbons, a clear bright solution is usually obtained. On the other hand, when dissolved in a petroleum solvent, the solution is opalescent. In the latter case it is necessary to postulate the presence of small particles having a different refractive index from that of the solvent. As rubber gives a substantially clear solution in benzene, it follows that the foreign particles are invisible and must, therefore, possess the same refractive index as this solvent or one very close to it.

OPACITY IS CAUSED BY PARTICLES IN SUSPENSION AND VARIES WITH DIFFERENT SPECIMENS

In the course of work on photogels a large number of rubber sols were prepared from different rubbers in different solvents. The relative clarity or opacity of the sols were noted, and some conclusions were drawn as to the nature of the particles in suspension. The relative transparency or opacity of a substance in suspension or colloidal dispersion depends on the size and shape of the particles. These first become apparent and are just visible in a Tyndall light beam when their size is small compared to the wave length of light. The visibility increases with the size, and the strongest opalescence is produced by particles of about 0.4 μ radius, if the particles are assumed to be spherical[1]. This enhanced effect is lost as the particles increase in size and reach a radius of 0.9 μ, after which the effect is relatively constant. With large particles, reflection and refraction come into play and become important with flat surfaces, as in tabular crystals. Consequently with particles of a great variety of shapes and sizes, such as we may expect to meet with in rubber sols, any calculation of particle number based on opacity is impossible. The present observations are therefore purely qualitative. The literature contains no detailed reference to this matter, nor any suggestion as to the cause of the differences in clarity. These are found to depend both on the solvent and on the type or method of preparation of the rubber. In the first instance two samples of crepe, 0.25 g. each, were sealed under reduced pressure with 10 cc. of solvent. The rubber was then dissolved by periodical shaking in the dark over two or three days until completely dispersed. One series was prepared with ordinary Malayan lace crepe; the other from a sample of purified crepe[2]. This latter had a low nitrogen content, and was prepared by treating ammoniated latex on the plantation with an enzyme and activator, centrifuging, and coagulating at a low dry rubber content. The two specimens of crepe were both very pale; the purified was a little lighter in color.

The order of opacity of the two series of sols was the same in both crepe specimens in the following solvents. These are given in order, beginning with the solvent giving the most opaque solution: ligroin, cyclohexane, cyclohexene,

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carbon tetrachloride, decalin, toluene, xylene, tetralin, benzene. This also is the order of increasing refractive index of these solvents. Throughout, the purified crepe gave less opaque solutions than the commercial crepe.

RELATIONSHIP OF REFRACTIVE INDICES OF RUBBER AND SOLVENTS

The refractive index of benzene is given as 1.501 and of rubber as $n_D^{25} = 1.519$[3]. These chemists found that the nonhydrocarbon components, such as proteins, which are insoluble in the rubber, have no effect on the refractive index. Further, the resins were found to have a very slight effect because they have approximately the same index as rubber.

It is apparent that the opacity decreases the nearer the refractive index of the solvent approaches the figure 1.519. This seemingly indicates that undispersed rubber in some form is responsible for the opacity. The relative opacities of the two crepe sols indicates that purified, low-nitrogen crepe contains fewer insoluble or undispersed particles than does commercial crepe.

It is well known that unmilled rubber hydrocarbon is not completely dispersed in any organic solvent in the dark; there remains undispersed the higher molecular or gel component; also, that different solvents dissolve different proportions of the hydrocarbon. Thus a gel remaining from the solvent action of a low boiling paraffin or ethyl ether is partially soluble in benzene; that is, the different solvents have different dispersing powers.

OPACITY MAY ARISE FROM INCOMPLETE DISPERSION

It follows, therefore, that a solution of an unmilled rubber in a solvent obtained by agitation of the rubber with the solvent, as in the crepe specimens considered above, must contain, dispersed throughout its volume, a large number of small particles of swollen gel. These might give rise to opacity if the refractive index depends on molecular complexity. That such particles are present can easily be demonstrated in the case of very difficultly soluble rubber, such as evaporated latex films. Such solutions are heterogenous to the naked eye. In petroleum ether the particles are visible. In benzene they are invisible, but may be detected on the surface of the vessel where the sol has drained away; for instance, on inverting a partially filled test-tube, tiny gelatinous particles are visible on the walls. If a little methylene blue is added to the latex before evaporation and the excess of dye removed by soaking, the insoluble, *e.g.*, the high molecular particles, appear to retain the dye more tenaciously than the lower ones when immersed in a solvent[4]. In benzene a darker layer of insoluble particles settles to the bottom of the vessel, the supernatant solute being lighter. With carbon tetrachloride, the darker layer forms on the surface.

OPACITY VARIES INVERSELY AS THE NITROGEN CONTENT

But these considerations afford no explanation of the paucity of insoluble particles in purified crepe. A variety of rubber specimens were examined, both raw and milled, and also purified in various ways. Acetone extraction had no effect on the transparency. Therefore, as the observations of McPherson and Cummings[3] would lead one to expect, the acetone solubles can be ignored in this regard. Milling has little or no effect[5]. Solutions of crepe

rubber, whether raw, ordinarily milled or dead-milled, were generally indistinguishable, provided sufficient solvent was used to give apparently complete dispersion. Diffusion fractions, whether from sheets or crepe, gave clear or almost clear sols in every solvent, including petroleum ether. The heterodisperse condition of the hydrocarbon consequently affords no solution of the problem. The opacity must therefore arise from nonhydrocarbon impurities in the form of a dispersion in the solution. This view is further confirmed by the opacity of rubber swollen but undispersed in solvents. Petroleum ether is a convenient solvent or swelling agent to give the maximum opacity, as this has the lowest refractive index of any of the usual solvents. The greatest opacity is shown by evaporated latex film or sprayed latex (whole rubber). Smoked sheet, fine para and ordinary crepes, both air- and oven-dried, are less opaque. Purified rubber from latex which has been centrifuged, creamed, dialyzed, or treated with protein-digesting enzymes or a combination of these, all give gels of less opacity, while the various fractions of diffusion rubber from smoked sheet give clear bright sols and gels.

RELATIVE TRANSPARENCY RELATED TO REFRACTIVE INDEX OF SOLVENTS

The fractions prepared by diffusion into petroleum ether give slightly clearer sols than those obtained by diffusion into benzene or carbon tetrachloride, but none of the rubbers purified in latex form gives sols as clear as those obtained with diffusion rubber. As these are free of solvent-insoluble protein, or substantially so (if sheet rubber is used) and the sediment is undisturbed, and as rubber from variously purified latex contains less nitrogen than the commercial grades and diffusion rubber hardly any, all the evidence tends to show that the opacity, whether in rubber sols or swollen gels, is caused by particles of protein or other nonhydrocarbon matter dispersed in the solvent. Smoked sheet usually contains about 0.4 to 0.5; crepe about 0.4; crepe from centrifuged latex about 0.2; crepe from centrifuged creamed latex 0.11; after washing and crepeing 0.09; crepe from double-creamed latex 0.15; crepe from electrodecanted latex 0.13 to 0.10; crepe from enzyme-digested latex 0.12; and diffusion rubber in benzene about 0.05 per cent of nitrogen. That is, the higher the proportion of nitrogen in the rubber, the more opaque the solution.

Washing coagulum and milling dry rubber breaks up the protein network which derives from the protein films surrounding the latex particles. If it reduces a substantial part of the protein to a fine state of subdivision, it should, as already explained, yield a more opalescent sol than would be obtained from unmilled rubber, always assuming that the subdivision does not go too far and reduce the particle size to much less than about 0.4 μ radius.

To put this to the test, tubes were prepared with raw crepe in petroleum ether, and the same crepe after mastication, both moderately milled and dead-milled. The differences were slight. In one case the dead-milled crepe was the most opaque and the unmilled crepe the least; in other cases no difference could be detected.

In a final series of experiments, a more concentrated dispersion or swelling of rubber in solvent was employed, using 0.5 gram of crepe rubber per 10 cc., and a wider range of solvents. Vigorous shaking was necessary to obtain sols of uniform appearance. The order of opacity is shown below, with the corre-

sponding refractive indices of the solvents, the last giving a clear, bright solution.

Solvent	Refractive index (20° C)
Ligroin (b.p. 60°–80°)	1.380
Carbon disulfide	1.630
Cyclohexane	1.424
Ethyl bromide	1.424
Dichloroethylene	1.449
Cyclohexene	1.446
Chloroform	1.445
Carbon tetrachloride	1.461
Decalin	1.483
Tetralin	1.480
Xylene (commercial)	1.497
Toluene	1.496
Monochlorobenzene	1.525
Ethyl iodide	1.522
Benzene	1.501

REFRACTIVE INDEX OF PROTEIN IN RUBBER CLOSE TO THAT OF BENZENE AND CLOSE TO THAT OF RUBBER ITSELF

From these figures it is apparent that the refractive index of the insoluble protein approaches most closely to that of a rubber sol in benzene. Sols of monochlorobenzene and ethyl iodide give slightly more opalescent sols than benzene, indicating that the refractive index of the protein complex is slightly lower than 1.522. The considerable opalescence of the carbon disulfide sol indicates that the refractive index of the protein is much below 1.630, for the same reason. Obviously the refractive index of the rubber sol will not be exactly that of the solvent, owing to the influence of the rubber itself; but the effect produced by the same small percentage of rubber hydrocarbon in the solvent should be at least approximately the same in all cases. A figure for the ref. index of a benzene sol is given by Shacklock[6], from which it is calculated that raising of the refractive index by dissolving 0.5 gram in 10 cc. of benzene amounts to an increment of 0.0126. If, therefore, we take the refractive index of the protein debris in a raw rubber sol as equal to that of a solvent giving the most transparent solution when 0.5 gram is dissolved in 10 cc. of solvent, we obtain a figure of approximately 1.501 + .0126 = 1.514. This figure is very close to that of rubber itself which is given as 1.519[3], and explains the transparency of raw rubber in mass, such as milled crepe (unfrozen), although it contains at least two or three per cent of a foreign substance (protein complex) dispersed in it. Only by staining can the protein be revealed photomicroscopically[7].

There are no figures available for the refractive index of latex proteins or for dried latex serum; nor are any figures for proteins to be found in the International Physical Tables. The protein-containing films are not likely to consist of protein alone. In the course of solidification, salts, sugars, quebrachitol and other water-soluble substances may be absorbed and will have their effect on the refractive index.

It was suggested long ago by Spence[8] that the protein in latex was closely associated with the hydrocarbon as a glycoprotein. This has not been confirmed. Tristram[9] has isolated and analyzed a protein from crepe rubber. Comparison of the amino acids separated with those obtained from latex serum led him to conclude that this is the only protein in latex. It would be interesting to have the refractive index of this protein.

WHY CLEAN RAW RUBBER IS TRANSPARENT

Conclusions.—As solutions of raw or slightly milled rubber may contain in suspension fine particles of undispersed rubber, and as the refractive index of rubber and that of benzene are almost the same (1.519 and 1.501, respectively, or 1.514 when the effect of the dissolved rubber is taken into account), the opacity in solvents of greater or less refractive index than 1.519 might be explained by the presence of small undispersed particles of rubber. As, however, dead-milled rubber sols are at least as opaque as, if not a trifle more opaque than, raw rubber sols, and as diffusion rubber is substantially transparent in all solvents, it is more probable that the opacity arises from some substance dispersed in rubber sols which is removed by purification of the raw rubber and is completely or almost completely absent in diffusion rubber. There seems little doubt but that this substance is the protein complex or whatever it may be, which forms the insoluble component of all rubbers. As the refractive index of this component must be very close to that of the rubber hydrocarbon, clean raw rubber is substantially transparent.

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THE MECHANISM OF THE ACTION OF MERCAPTOBENZOTHIAZOLE AND OF ITS DERIVATIVES IN THE VULCANIZATION PROCESS *

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It is a well known fact that mercaptobenzothiazole and its derivatives, as well as other types of organic compounds, accelerate vulcanization only in the presence of metallic oxides (activators)[1]. This is true in general of compounds containing a thiol (-SH) group, as well as of compounds where a thiol group is formed as the result of a chemical change during the process of vulcanization. Among metallic oxides, zinc oxide is most frequently used as an activator.

Likewise, organic accelerators in general not only hasten the process of vulcanization, completing it often in a few minutes, but also improve considerably the mechanical properties of the vulcanizates.

The mechanism of vulcanization has been the subject of numerous investigations, in which considerable attention has been paid to mercaptobenzothiazole and its derivatives. The first experimental work in this field was by Sebrell and Boord[2], who showed that the acceleration of vulcanization in the presence of such compounds depends on the thiol group and also in part on the sulfur atom in the thiazole ring.

Different views have been advanced as to the role played by the thiol group. We shall confine ourselves to a discussion of the action of compounds of the R—SH type, in the presence of zinc oxide.

The earliest theory, advanced by Bruni and Romani[3], assumes the following mechanism in the case of mercaptobenzothiazole:

$$2\,R{-}SH + ZnO \rightarrow R{-}S{-}Zn{-}S{-}R + H_2O$$
$$x(R{-}S{-}Zn{-}S{-}R) + S_x \rightarrow x(R{-}S{-}S{-}R) + x(ZnS)$$
$$R{-}S{-}S{-}R \rightarrow R{-}S{-}R + S_{(active)}$$

Later this view was extended to include substituted thioureas, such as thiocarbanilide, *i.e.*, compounds capable of reacting in tautomeric form and giving rise to an —SH— group.

However, this theory proved to be not entirely adequate, although by means of it, it has been possible to predict correctly the formation of a zinc salt of mercaptobenzothiazole and of dibenzothiazyl disulfide[4]. The theory does not explain the fact, as has been pointed out by Sebrell and Boord[2] and later by Kindscher[5], that dibenzothiazyl disulfide is a less active accelerator than mercaptobenzothiazole itself. Furthermore, our experiments have shown that the disulfide does not change into the monosulfide, as would be expected from the theory of Bruni and Romani; on the contrary the monosulfide forms the disulfide.

According to Bedford and Sebrell[6], the mechanism of the action of accelerators of the R—SH type is linked with the formation of zinc salts. The purpose of these, they believe, is to transform elemental sulfur into its active

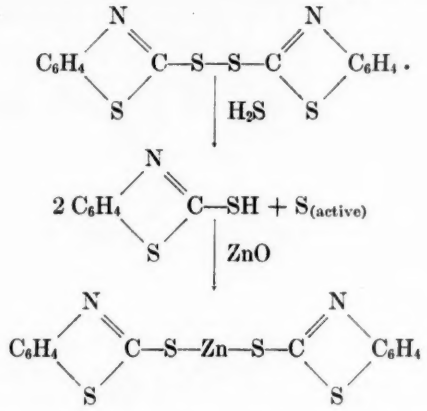
* An original contribution from the Lomonossov Institute of Chemical Technology, Moscow, U.S.S.R.

form, according to the following series of reactions:

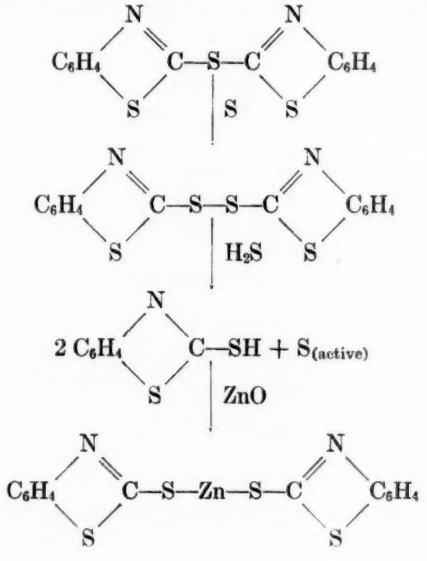
$$2\ R{-}SH + ZnO \rightarrow (R{-}S)_2Zn + H_2O$$
$$(R{-}S)_2Zn + S_x \rightarrow (R{-}SS_x)_2Zn$$
$$(R{-}SS_x)_2Zn \rightarrow (R{-}S)_2Zn + xS_{(active)}$$

While studying the transformation of the disulfide and of the monosulfide of mercaptobenzothiazole under vulcanizing conditions, it was proved that they are changed into mercaptobenzothiazole and into the zinc salt[7]. Neither of the theories mentioned above explains this fact satisfactorily.

We believe that the following mechanism explains the nature of the conversion of the disulfide and the monosulfide into mercaptobenzothiazole. The disulfide changes into mercaptobenzothiazole, which then forms the zinc salt in accordance with the following reactions which take place during vulcanization:

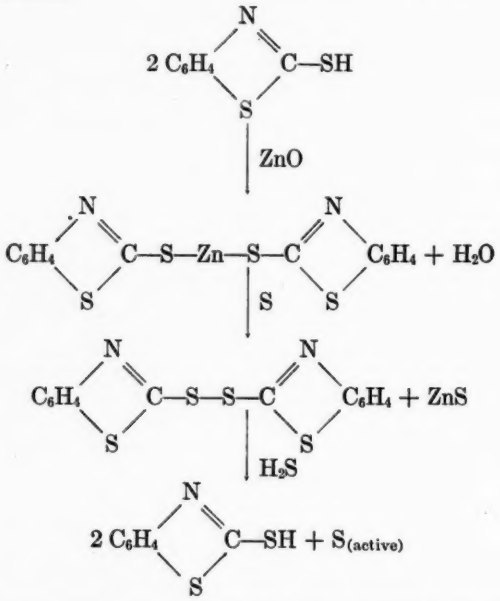


For the monosulfide, the following series of reactions have been suggested:



The final stage in these reactions is the formation of the zinc salt. Its specific function, however, remains uncertain. After succeeding in preparing a zinc mercaptide of normal composition, data were obtained which make it possible to interpret the function of the zinc salt[8]. It was shown that, under vulcanizing conditions, the zinc salt changes into mercaptobenzothiazole. The latter, in turn, reacts with more zinc oxide, forming the zinc salt anew[9].

This interaction can be explained easily by assuming the following mechanism for the reactions:

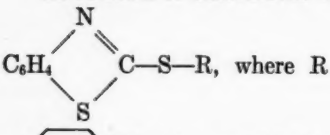
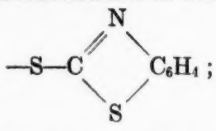
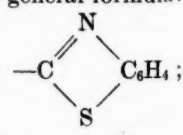
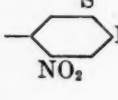


The active sulfur formed brings about the vulcanization of rubber.

It should be noted here that, aside from the active sulfur formed in the way mentioned above, the vulcanization of rubber may be brought about also by polysulfides. The possibility of formation of such polysulfides from disulfide and sulfur has been pointed out by Langenbeck and Rheim[10].

It is not impossible that the zinc salt itself plays a part in the formation of active sulfur by virtue of unstable intermediary products formed by the addition of elementary sulfur to the zinc salt. The tendency of the zinc salt to undergo addition reactions generally[11] speaks in favor of the formation of such intermediary products.

With respect to derivatives of mercaptobenzothiazole containing substituents in the benzene ring, the mechanism of their action would follow an analogous scheme.

The action of derivatives of mercaptobenzothiazole of the general formula:  where R may be:  ;  ;  etc., would also follow the mechanism of the above mentioned

reactions. Under vulcanizing conditions they split, forming mercaptobenzothiazole[12], which in turn accelerates vulcanization.

EXPERIMENTAL PART

1. *Preparation of vulcanized samples and examination of the acetone extracts.* The mixtures in the following table were prepared on a laboratory mixing mill.

TABLE

Formulation	Compounds (1)	Compounds (2)
Smoked sheet	100.0	100.0
Sulfur	2.0	2.0
Zinc salt	2.5	2.5
Zinc oxide	...	2.5

The mixtures were cured in a press for 1 hour at 140° C. After vulcanization, the sheets were passed through a mill, were then cut into narrow strips, and were extracted with acetone in a Soxhlet extractor for approximately 10 hours. The acetone was distilled off, and mercaptobenzothiazole was separated from the brownish resinous residue by fractional crystallization. Fine white needles of bitter taste, soluble in water and in weak ammonia, were obtained. The melting point was 174° C.

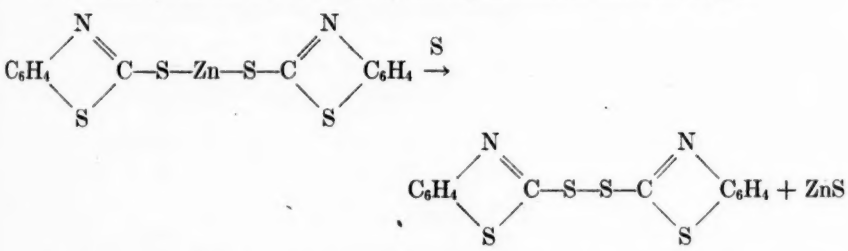
Ninety-two grams of specimen (1) yielded 0.66 gram, and 78 grams of specimen (2) yielded 0.34 gram of mercaptobenzothiazole.

ANALYSIS

Sulfur determined by the Carius method

0.1535 gram substance:	0.4270 $BaSO_4$
0.1790 gram substance:	0.4962 $BaSO_4$
Sulfur found in %:	38.22 and 38.10
Sulfur calculated in % from $C_7H_5NS_2$	38.37

2. *Reaction between the zinc salt of mercaptobenzothiazole and sulfur.*



Two grams of the zinc salt of mercaptobenzothiazole and 0.1 gram of sulfur were dissolved in xylene which had been dried over sodium and redistilled. The xylene solution was boiled for 3 hours on an oil bath. Due to partial resinification, the solution turned brown. While still hot, the xylene solution was filtered to separate the sediment formed. Zinc sulfide and unreacted zinc salt were found in this sediment. These were separated by heating the sediment with a 2.5 per cent sodium hydroxide solution. In this way, the zinc salt was split by the alkali and went into solution. The remaining zinc sulfide was filtered, washed with ammonia and water, and dried. A weight of 0.11

gram of zinc sulfide was obtained. On treatment with hydrochloric acid, this dissolved completely, with evolution of hydrogen sulfide.

Contrary to expectation, mercaptobenzothiazole and a small quantity of dibenzothiazyl disulfide were separated from the xylene solution. The following procedure was used:

The xylene was distilled off under vacuum. The brownish residue was treated with boiling benzene, which resulted in the major portion of it going into solution. The solution was filtered, the benzene was driven off, and the residue was treated several times with boiling water to extract the mercaptobenzothiazole. The water extracts were collected and evaporated to a small volume. On standing, mercaptobenzothiazole crystallized out. After recrystallizing from benzene, the melting point was 174° C. The yield was 0.32 gram. From the water-insoluble residue, 0.02 gram of dibenzothiazyl disulfide was separated, and, after recrystallization from benzene, had a melting point of 177–178° C.

SUMMARY

In our work we confirmed that, in the process of vulcanization of rubber, the normal zinc salt of mercaptobenzothiazole changes into mercaptobenzothiazole.

Based on this and on other facts described earlier, a probable mechanism of the action of mercaptobenzothiazole and its derivatives in the vulcanization of rubber is suggested.

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UNSATURATION OF BUTADIENE AND RELATED POLYMERS

AS DETERMINED BY IODINE CHLORIDE ADDITION *

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Since iodine chloride adds quantitatively to the double bonds in natural rubber hydrocarbon[1], it was considered important to study the reaction of various unsaturated synthetic elastomers with this reagent. Recently Cheyney and Kelley[2] found that Wijs reagent reacted so slowly with polybutadiene and its copolymers swollen in chloroform or carbon disulfide that the addition reaction required 48 hours or longer to approach completion. Butadiene and butadiene-styrene polymers are frequently only partially soluble in chloroform or carbon disulfide and, if soluble, they are partially precipitated by the addition of the glacial acetic acid in Wijs reagent. This requires that the reaction proceed between the swollen polymer and the iodine chloride solution, which accounts in part for the long period needed to complete the reaction. Other complications, such as emulsion formation and occlusion of iodine in the precipitate during titration of the unreacted iodine chloride, are likely to be involved in the standard Kemp-Wijs procedure[3] which was developed for natural rubber.

The present investigation was undertaken to overcome these difficulties and to develop a rapid and accurate method which could be applied to various types of synthetic rubber-like polymers. It was hoped also that data obtained on the unsaturation of these polymers would throw some light on their chemical structure as related to polymerization procedure.

A study of numerous solvents showed that *p*-dichlorobenzene heated from 165° to 172° C was the most satisfactory for general use. Cheyney and Kelley[2] objected to this solvent on the ground that cyclization of synthetics takes place as the result of heating. The results of the present investigation show, however, that very little loss of unsaturation occurs in the polymers during the heating in *p*-dichlorobenzene necessary for a complete solution. The use of *p*-dichlorobenzene is also advantageous for use with crude natural rubber, since solution is complete in less than one hour, which is important in the tougher and less soluble types. The present authors have confirmed the finding of Blake and Bruce[4] on the superiority of this solvent for vulcanized rubber compared with tetrachloroethane[5]. Soft vulcanized butadiene-styrene copolymers are soluble also in hot *p*-dichlorobenzene, making it possible to determine the total rubber content of a soft vulcanized mixture of natural and GR-S rubber.

To avoid or substantially to reduce precipitation on addition of Wijs solution, the iodine chloride was made up using carbon tetrachloride as a solvent in place of glacial acetic acid. In the case of the butadiene-nitrile copolymers the standard Wijs solution was employed, since the iodine chloride reaction product was more soluble in the presence of the glacial acetic acid.

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Emulsions which formed during titration were broken by the addition of 25 cc. of alcohol. In the case of vulcanized GR-S tire tread stocks containing channel black, it was found that, by omitting the water and adding 75 cc. of alcohol, excellent results were obtained. In this case the presence of the larger quantity of alcohol caused the carbon black to settle rapidly, so the end-point could be quickly obtained.

In the case of polybutadiene, 0.10-gram samples gave low results, since the excess of iodine chloride is not sufficient to complete the reaction. Sample weights of 0.06 gram were found to give consistent results. In the case of the high-nitrile type of polymer, solution in *p*-dichlorobenzene is difficult; 20 to 60 passes through a clean, tight mill before extraction greatly aids solution. This milling has been found to have no significant effect on the iodine value of any of the synthetics or of natural rubber, and can be practiced to advantage whenever the polymer requires too long a period to dissolve.

GENERAL RECOMMENDED PROCEDURE

Unless otherwise purified, samples are acetone-extracted in the standard manner for 16 hours, in the absence of strong light. In the case of vulcanized samples, this is followed by a 4-hour chloroform extraction. The extracted samples are freed from solvent by heating to constant weight in an oven at 70° C under vacuum, cut into fine pieces (approximately 15-mesh), and preserved under nitrogen or in high vacuum before analysis to prevent oxidation.

The finely divided sample (0.10 gram, or 0.06 gram in case of polybutadiene) is placed in a 500-cc. Pyrex glass-stoppered vapor-release iodination flask with 50 grams of pure *p*-dichlorobenzene. The flask with contents is placed on a hot plate at a temperature of 175° to 185° C, with the vapor release on the iodine flask lined up properly to release the pressure that is formed during heating. It is desirable to cover the sides of the flask with an asbestos shield to prevent the solvent from solidifying in the upper part of the flask. The contents of the flask are gently whirled from time to time to facilitate solution, care being taken to avoid causing particles to adhere and scorch on the sides of flask above the solvent. The time for solution depends on the nature of the polymer, and usually varies from about 20 to 180 minutes. If the time required exceeds 3 hours and a rubber mill is available, it is recommended that the polymer be milled to increase its solution rate.

Following solution, the flask with its contents is removed and allowed to cool to room temperature. Before crystallization of the *p*-dichlorobenzene is complete, the partially solidified solution is liquefied by adding 50 cc. of chloroform. Twenty-five cubic centimeters of iodine chloride in carbon tetrachloride is added from a pipet, using a vacuum to suck the solution up uniformly and very slowly to avoid loss of iodine chloride by evaporation. A thin film of 15 per cent potassium iodide is placed on the stopper of the iodine flask just before closing, and the solution allowed to stand for one hour at room temperature in the dark to complete the reaction. Twenty-five cubic centimeters of 15 per cent freshly prepared potassium iodide solution is added, followed by the addition of 50 cc. of distilled water. The excess iodine is immediately titrated with standard 0.1 *N* sodium thiosulfate solution, using freshly prepared starch indicator, which is added towards the end of the titration. Twenty-five cubic centimeters of ethyl alcohol are added towards the end of the titration to break the emulsion.

The end-point is reached when the color change passes from a light brown to a light purple and finally to a colorless solution. When the end-point is

near, moderate shaking of the solution is necessary after each drop or partial drop of sodium thiosulfate is added. Violent shaking should be avoided to prevent breaking the flask. A blank is carried through all the operations of heating, etc. The difference in cubic centimeters of 0.1 N thiosulfate between the blank and the sample titration is used to calculate the iodine value:

$$\text{Iodine value} = \frac{\text{cc. of 0.1 } N \text{ } Na_2S_2O_3 \times 1.2692}{\text{wt. of sample in grams}}$$

IODINE VALUE OF POLYBUTADIENE

The effect of using different solvents on the iodine value of polybutadiene (German sodium Buna-85) under various conditions is shown by Table I.

TABLE I

EFFECT OF VARYING EXPERIMENTAL CONDITIONS OF IODINE VALUE OF POLYBUTADIENE

Solvents employed	Polybutadiene (gram)	Heating period in $C_6H_4Cl_2$ (hours)	Iodine chloride solution used	Time of reaction (hours)	Iodine value
75 cc. of CS_2	0.1040	...	Wijs	3	399.0[a]
	0.1034	...	Wijs	24	407.9[a]
75 cc. of $CHCl_3$	0.1031	...	Wijs	3	388.1[a]
	0.1026	...	Wijs	24	406.3[a]
50 grams of $C_6H_4Cl_2$+ 50 cc. of CS_2	0.1201	1.0	CCl_4	1	385.3
	0.1017	1.0	CCl_4	1	413.7
	0.1014	1.0	CCl_4	1	412.6
	0.0824	1.0	CCl_4	1	435.7
	0.0756	1.0	CCl_4	1	436.5
	0.0759	1.0	CCl_4	1	436.1
50 grams of $C_6H_4Cl_2$+ 50 cc. of $CHCl_3$	0.0753	1.0	CCl_4	1	435.0
50 grams of $C_6H_4Cl_2$+ 50 cc. of CS_2	0.0668	1.0	CCl_4	1	438.6
	0.0615	1.0	Wijs	1	409.1
	0.0613	6.0	CCl_4	1	435.9
	0.0604	1.0	CCl_4	1	438.5
	0.0606	1.0	CCl_4	1	440.9
	0.0511	1.0	CCl_4	1	440.1
	0.0510	1.0	CCl_4	1	440.5
	0.0313	1.0	CCl_4	1	441.7
	0.0221	1.0	CCl_4	1	440.4
	0.0218	1.0	CCl_4	1	441.8

[a] Heavy precipitation occurs on adding Wijs reagent.

In the experiments where 0.1-gram samples are employed, the iodine values are too low because the addition reaction is not complete. Some precipitation occurred in all cases where solution was effected by hot *p*-dichlorobenzene, supplemented by carbon disulfide or chloroform, and where iodine chloride in carbon tetrachloride was used. Where heavier precipitation occurred using Wijs solution, the increased time of reaction did not overcome the low results. Heating for 6 hours in *p*-dichlorobenzene resulted in about 1 per cent reduction in the iodine value. This shows that the effect on the unsaturation as the result of heating for 1 hour in *p*-dichlorobenzene can be disregarded.

Since excess iodine chloride appeared important, a series of determinations was carried out by varying the sample weights. The samples were dissolved

in 50 grams of boiling *p*-dichlorobenzene for 1 hour, 50 cc. of carbon disulfide and 25 cc. of 0.2 *N* iodine chloride in carbon tetrachloride were added, and the reaction was carried out for 1 hour at room temperature. The results, plotted in Figure 1, show that a weight of sample of 0.05 to 0.06 gram is satisfactory. These weights correspond to an excess of iodine chloride of 50 to 60 per cent. About the same excess was found to be necessary to complete the iodine chloride reaction in 1 hour in the case of natural rubber[6].

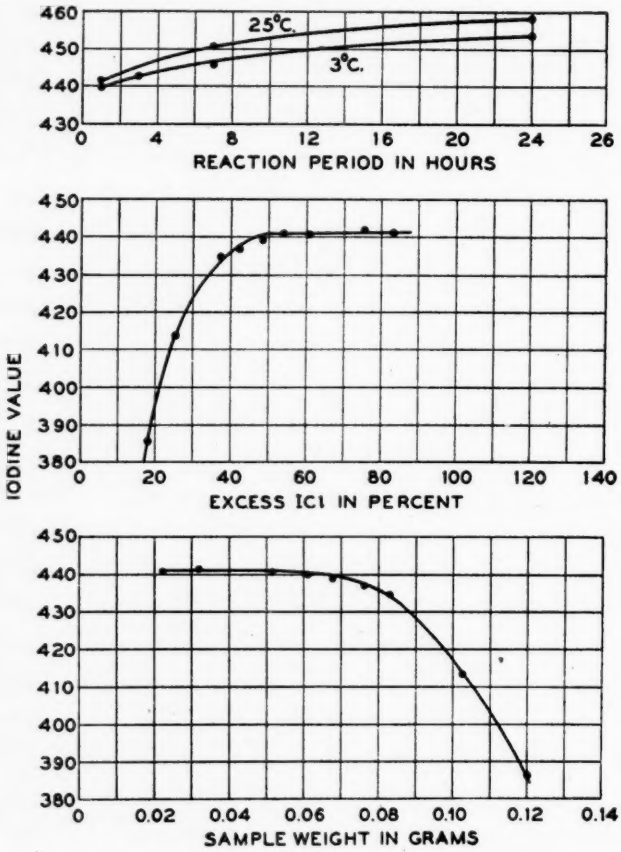

FIG. 1.—Iodine value of polybutadiene.

To determine the tendency of polybutadiene to substitute, a series of determinations was carried out at room temperature and at 3° C, with variations in reaction periods from 1 to 24 hours. The sample weight was 0.06 gram and the procedure the same as the other series shown in Figure 1. Figure 1 indicates that substitution takes place slowly even at 3° C. A reaction period of 1 hour, therefore, appears to be justified, since the addition reaction apparently is completed in this period, provided the proper excess of reagent is employed. The high iodine values obtained by Cheyney and Kelley[2] after a reaction period of 336 hours are due undoubtedly in part to substitution.

The theoretical iodine value for polybutadiene is 469.6. The acetone-extracted sodium butadiene polymer was not a pure hydrocarbon, judged from its combustion analysis. The nonhydrocarbon portion appears to be made up largely of ash and combined oxygen.

Two butadiene and one isoprene emulsion polymers were prepared under the supervision of B. S. Biggs of these laboratories. The latex was coagulated by pouring it into an excess of alcohol, and the coagulum was washed in warm 50 per cent alcohol and finally in pure alcohol. It was finally dried to constant weight under a high vacuum at 60° C. A highly purified lot of isoprene was also polymerized by the soap emulsion method.

The iodine values and analysis of these polymers are given in Table II in

TABLE II

COMBUSTION ANALYSES AND IODINE VALUES OF BUTADIENE AND ISOPRENE POLYMERS

Polymer	Carbon (%)	Hydrogen (%)	C/H ratio	Iodine value	Theoretical iodine value (%)
Polybutadiene (German Na 85)[a]	88.08	10.87	8.10	440.5	93.7
Polybutadiene (emulsion method)	88.86	11.21	7.93	455.1	96.6
Polyisoprene (emulsion method)	...	...	...	369.1	99.0

[a] Acetone-extracted before analysis.

comparison with the acetone-extracted German Buna 85 viscosity polymer made by mass polymerization, using sodium as a catalyst. Whereas the German sodium polymer of butadiene has an iodine value somewhat below the theoretical value, the unsaturation of the emulsion polymers agreed fairly closely with theory.

The iodine value of 440 for the extracted sodium Buna-85 is lower than theory, which is 469.6, even when the nonhydrocarbon portion is considered. The unsaturation of sodium Buna-85 is calculated to be 93.69 per cent of theory. This low unsaturation value, together with its low solubility and plasticity, may be taken as evidence of the presence of some type of interlinkage between the polymer chains; however, knowledge of these structural details is lacking. Chain branching, oxygen bridging, or cyclization during polymerization has been suggested to account for the differences in the properties of butadiene and isoprene polymers, compared with natural rubber.

IODINE VALUE OF BUTADIENE-STYRENE COPOLYMERS

The effect of using different solvents and experimental conditions on the iodine value of an acetone-extracted 75/25 butadiene-styrene copolymer is shown in Table III. These results indicate that the use of either chloroform or carbon disulfide to supplement *p*-dichlorobenzene is satisfactory, provided iodine chloride in carbon tetrachloride is employed in place of Wijs solution. Chloroform, however, is preferred over carbon disulfide because of the objectionable odor and fire hazard of the latter solvent.

Data from Table II, plotted in Figure 2, show evidence of very little substitution in the case of the butadiene-styrene copolymer. Reaction conditions of 1 hour at room temperature appear to be a satisfactory selection when iodine chloride in carbon tetrachloride is employed. The use of Wijs solution

TABLE III

IODINE NUMBER OF A BUTADIENE-STYRENE COPOLYMER UNDER VARIOUS EXPERIMENTAL CONDITIONS

Solvents employed	Butadiene-styrene copolymer (gram)	Heating period in $C_6H_4Cl_2$ (hours)	Iodine chloride solution used	Temp. of reaction (° C)	Time of reaction (hours)	Iodine value
75 cc. of $CHCl_3$	0.10	...	Wijs	20–30	48	334.1[a]
75 cc. of CS_2	0.10	...	Wijs	20–30	48	330.0[a]
50 grams of $C_6H_4Cl_2$+ 50 cc. of CS_2	0.10	1.0	Wijs	26	1	319.3
	0.10	1.0	Wijs	26	3	330.2
	0.10	1.0	Wijs	26	7	336.0
50 grams of $C_6H_4Cl_2$+ 50 cc. of $CHCl_3$	0.10	1.0	Wijs	26	7	335.8
50 grams of $C_6H_4Cl_2$+ 50 cc. of CS_2	0.05	1.0	CCl_4	29	1	343.5
	0.10	1.0	CCl_4	29	1	343.5
50 grams of $C_6H_4Cl_2$+ 50 cc. of $CHCl_3$	0.10	1.0	CCl_4	29	1	344.0
50 grams of $C_6H_4Cl_2$+ 50 cc. CS_2	0.10	6.0	CCl_4	29	1	343.2
	0.10	1.0	CCl_4	29	3	345.4
	0.10	1.0	CCl_4	29	7	345.5
	0.10	1.0	CCl_4	3	1	342.2
	0.10	1.0	CCl_4	3	3	344.0
	0.10	1.0	CCl_4	3	7	343.8

[a] Solid phase present throughout reaction.

gives low results, even after a 48-hour reaction period. Under these conditions the iodine values obtained are in agreement with those of Cheyney and Kelley[2]. The data in Figure 2 show that Wijs solution is unsatisfactory for use with butadiene-styrene copolymers, whereas iodine chloride in carbon tetrachloride appears to meet the necessary requirements. Iodine bromide (Hanus solution)

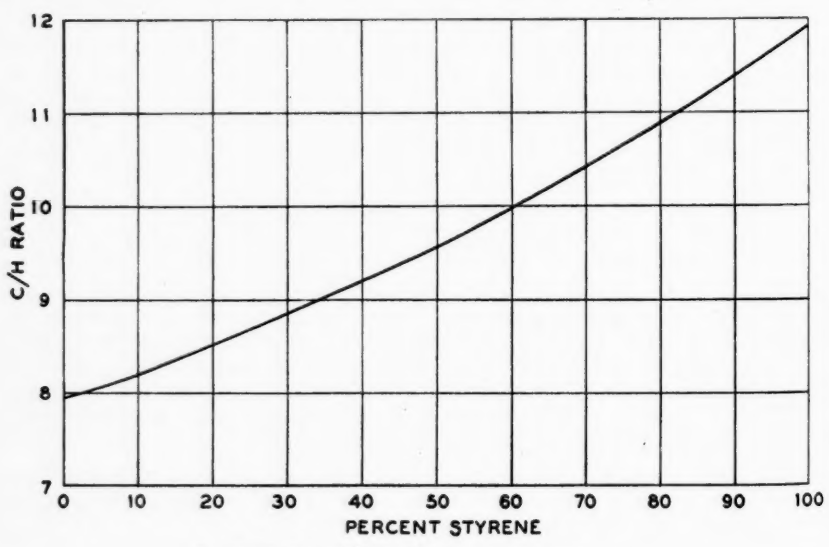

FIG. 2.—Iodine value of butadiene-styrene copolymers.

was also tried, but was found to be slower than Wijs solution under identical conditions. After 7 hours' reaction period, the Hanus value was 318, in contrast to 336 for the Wijs value for the same period.

REACTIVITY OF DOUBLE BONDS IN BUNA-S

Since some of the double bonds in Buna-S appear to be located in side-chain vinyl groups as a result of 1.2 addition polymerization of the butadiene, it was thought that this might affect their reactivity, compared with the double bonds in the main chain resulting from 1,4 addition. To detect such a difference, the

TABLE IV

RELATIVE REACTIVITY TOWARDS HALOGENS OF BUNA-S AND RUBBER[a]

Polymer	0.2 *N* Addition agent added	Reaction period (min.)	Reagent consumed (cc.)	Addition agent consumed (%)
Rubber	25 cc. of I_2 in CCl_4	240	0.70	2.8
Buna-S	25 cc. of I_2 in CCl_4	240	0.56	2.3
Rubber	11 cc. of ICl in CCl_4	10	10.56	96.0
Buna-S	11 cc. of ICl in CCl_4	10	10.00	91.0
Rubber	5 cc. of ICl in CCl_4	10	4.90	98.0
Buna-S	5 cc. of ICl in CCl_4	10	4.88	97.5
Rubber	3 cc. of ICl in CCl_4	60	2.94	98.0
Buna-S	3 cc. of ICl in CCl_4	60	2.97	99.0
Rubber	3 cc. of IBr in CCl_4	10	1.90	63.2
Buna-S	3 cc. of IBr in CCl_4	10	1.90	63.2

[a] 0.1000 gram of acetone-extracted crepe or Buna-S dissolved in 75 cc. of chloroform and reaction carried out in dark at 25° C.

reactivity of Buna-S with iodine, iodine chloride, and iodine bromide was compared with rubber under identical conditions. These experiments are outlined in Table IV and the data show that very little difference exists between the reactivity of Buna-S and rubber hydrocarbons toward iodine, iodine chloride, or iodine bromide.

DETERMINATION OF STYRENE IN BUTADIENE–STYRENE COPOLYMERS

Since no method was available for the determination of the styrene content of GR-S rubber or other butadiene-styrene copolymers, the present authors employed combustion analyses, using the carbon-hydrogen ratio to calculate the styrene content. As the styrene content increases from 0 to 100 per cent, the carbon-hydrogen ratio will vary from 7.943 to 11.915, as shown in Figure 3. A variation of ±0.2 per cent in carbon will change the carbon-hydrogen ratio in a 21 per cent styrene–79 per cent butadiene copolymer by ±0.017, which is equivalent to ±0.5 per cent styrene. A variation of only 0.023 per cent in the hydrogen content will be equivalent to the same change in carbon-hydrogen ratio and styrene content; therefore, special precautions must be taken in the combustion analyses to avoid errors. The present authors depended on a carefully conducted micromethod combustion. These analyses were carried out by F. C. Koch of these laboratories. In the case of soap-free polymers, the accuracy is believed to be sufficient to establish the styrene content to within 1 or 2 per cent.

Data giving the variation of iodine value and per cent of theoretical unsaturation are shown in Table V and Figure 4 for copolymers of butadiene and

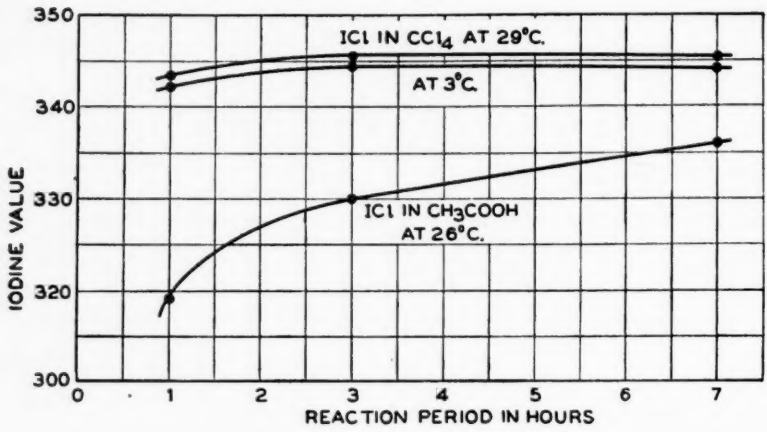

FIG. 3.

TABLE V

CARBON-HYDROGEN RATIOS, CALCULATED STYRENE CONTENTS, AND IODINE VALUES OF BUTADIENE-STYRENE POLYMERS

Polymer	Carbon (%)	Hydrogen (%)	C/H ratio	Styrene from C/H (%)	Iodine value	Styrene from I. V.[a] (%)	Theoretical unsaturation[b] (%)
1	89.00	10.39	8.56	21.0	360.0	23.4	97.0
2	88.28	10.34	8.54	20.8	342.0	27.2	91.9
3	88.65	10.44	8.50	19.0	357.8	23.9	94.0
4	89.00	10.36	8.59	22.0	338.2	28.0	92.3
5	89.04	10.40	8.56	21.0	341.2	27.4	92.0
6	89.70	10.42	8.61	22.5	334.0	28.9	91.8
7	88.08	10.36	8.50	19.0	352.8	24.9	92.7
8	88.85	10.37	8.58	21.6	342.0	27.2	92.9
9	88.35	10.31	8.56	21.0	343.1	27.0	92.2
10	88.38	10.28	8.60	22.2	340.0	27.6	93.0
11	89.09	10.32	8.63	23.2	343.5	26.9	95.2
12	88.52	10.29	8.61	22.7	356.7	24.1	98.3
13	89.52	10.13	8.84	29.6	313.4	33.4	94.8
14	89.27	9.83	9.08	36.4	291.1	38.1	97.4
15	89.47	9.59	9.33	44.0	234.0	50.0	89.0
16	89.80	8.81	10.19	66.0	142.4	69.8	89.2
				Purified polymers			
P-1[c]	89.24	10.28	8.68	25.0	353.5	24.8	100.4
P-2[c]	89.48	10.23	8.73	26.3	346.5	26.3	100.1
P-3[c]	89.34	10.25	8.72	25.8	353.3	24.8	101.3
P-4[d]	89.80	10.42	8.62	23.0	356.1	24.2	98.5
P-5[d]	89.87	10.32	8.61	22.7	359.3	23.6	98.7
P-6[d]	89.33	10.35	8.63	23.2	359.1	23.6	99.5
P-7[d]	89.26	10.25	8.70	25.3	359.8	23.5	100.3
P-8[d]	89.27	10.29	8.67	24.5	359.6	23.5	100.1
P-9[d]	88.76	10.35	8.58	21.9	355.5	24.4	97.0
P-10[d]	88.06	10.30	8.55	20.7	352.1	25.0	94.8

[a] $\%\ \text{styrene} = 100 - \left(\frac{\text{iodine value}}{469.6} \times 100\right)$.

[b] Calculated by employing 469.6 as the theoretical iodine value for polybutadiene—*i.e.*,

$$\frac{\text{iodine value of polymer} \times 100}{\text{wt. proportion of butadiene in polymer} \times 469.6} = \%\ \text{of theoretical unsaturation.}$$

[c] Prepared by coagulation of polymer emulsion with alcohol and washing with alcohol. Addition of antioxidant was omitted.

[d] Prepared from benzene-soluble soap-free commercial polymer No. 12 by fractional coagulation from dilute benzene solution upon addition of methyl alcohol. These fractions represent about 90 per cent of the polymer and are given in order of decreasing molecular weights.

styrene of different styrene contents. The largest group analyzed was the regular commercial polymer made by using charging ratios of 25 styrene and 75 butadiene. In all cases the styrene content was found to be somewhat less than the charging ratio. The values for polybutadiene in Figure 4 are those found for the sodium "85" viscosity polymer and for a purified benzene-soluble polybutadiene made by the emulsion process. Data on the latter polymer are given in Table III.

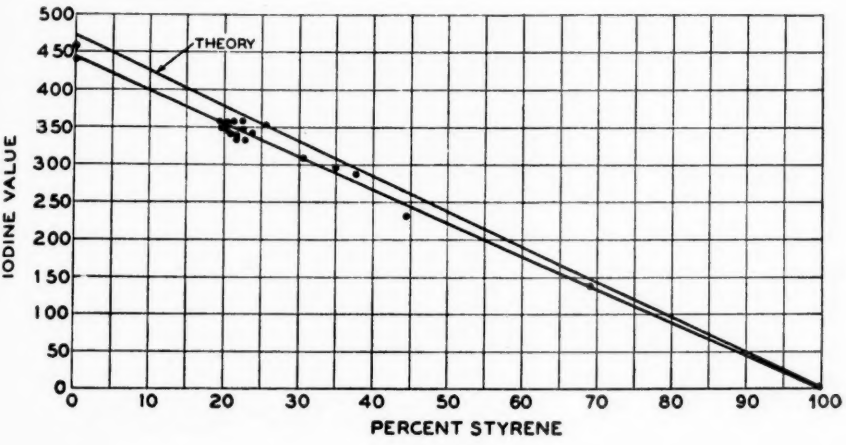

FIG. 4.

It is to be noted from Table V and Figure 4 that the iodine values of butadiene-styrene copolymers are approximately proportional to their styrene content. The iodine value can, therefore, be employed to calculate the styrene content. However, variations in the amount of unsaturation lost during polymerization and the presence of soap and other impurities influences the accuracy of such a procedure. The commercial emulsion polymers contain variable amounts of inorganic substances, their ash contents usually varying from 0.3 to 1.2 per cent. Combustion analyses indicate that they contain some combined oxygen, in some cases possibly as much as 0.2 to 0.5 per cent.

The data in Table V on purified polymers are evidence that there is very little loss in unsaturation in the butadiene beyond the one double bond per butadiene molecule which would result from linear chain polymerization. The data on the per cent of theoretical unsaturation for the butadiene present in the acetone-extracted commercial polymers are undoubtedly influenced somewhat by errors in the results for styrene content based on microcombustion analyses. These data indicate that 2 to 10 per cent of the theoretical unsaturation of the butadiene after one of its double bonds enters the chain is used up during the polymerization process. However, it was found, as shown in Table V, that by careful fractionation of a benzene solution of a soap-free benzene-soluble type polymer the unsaturations of the higher molecular fractions are close to the theoretical value. The whole polymer, No. 12 in Table V, was unsaturated to 98.3 per cent of theory. In this case the styrene content was determined by an interferometer method recently developed by W. O. Baker and J. H. Heiss of these laboratories, giving a styrene content of 23.4 per cent and a theoretical unsaturation of 99.1 per cent.

In the case of benzene-soluble emulsion-type polymers purified by coagulation and washing with ethyl alcohol, the data in Table V show that very little loss in the unsaturation of butadiene beyond one of its double bonds occurs during polymerization. In this case the styrene contents given were also checked by the above-mentioned interferometer method. The iodine values of the alcohol precipitated and purified emulsion polymers from pure butadiene and specially purified isoprene also showed close agreement with theory.

TABLE VI

IODINE VALUE OF BUTADIENE-NITRILE COPOLYMERS UNDER VARIOUS EXPERIMENTAL CONDITIONS

Solvents employed	Butadiene-nitrile copolymers (gram)	No. of passes through mill	Heating period in $C_6H_4Cl_2$ (hours)	Iodine chloride solution used	Time of reaction (hours)	Iodine value[a]
	(Copolymer containing 6.54% nitrogen)					
50 grams of $C_6H_4Cl_2$+ 50 cc. of CS_2	0.1	0	2.5	Wijs	1	315.3[b]
50 grams of $C_6H_4Cl_2$+ 50 cc. of $CHCl_3$	0.1	0	2.5	CCl_4	1	306.0[b]
	0.1	20	1.25	Wijs	1	302.1 (303.0)
	0.1	0	2.5	Wijs	1	300.0 (302.5)
50 grams of $C_6H_4Cl_2$+ 75 cc. of $CHCl_3$	0.1	0	2.5	Wijs	1	302.2
50 grams of $C_6H_4Cl_2$+ 50 cc. of $CHCl_3$	0.1	0	2.5	Wijs	3	300.5
	0.1	0	2.5	Wijs	7	306.0 (307.2)
	0.05	0	2.5	Wijs	7	306.2
	0.1	0	4.5	Wijs	1	300.1
50 grams of $C_6H_4Cl_2$+ 75 cc. of $CHCl_3$	0.1	0	4.5	Wijs	1	300.4
50 grams of $C_6H_4Cl_2$+ 50 cc. of $CHCl_3$	0.1	0	9	Wijs	3	239.0 (245.3)[c]
	0.1	20	3	Wijs	3	264.8 (263.8)
	0.1	60	2	Wijs	3	262.0
	0.1	60	1	Wijs	3	265.8
	0.05	60	1	Wijs	3	265.5
75 cc. of $CHCl_3$	0.05	60	...	Wijs	3	264.2
	0.05	60	...	Wijs	30	268.2

[a] Reaction carried out at room temperature.
[b] Heavy precipitate formed.
[c] Polymer undissolved.

Since soap is not removed by acetone extraction, its presence in the polymer reduces the iodine value. The soap content is generally less than 1 per cent, but in some cases more may be present. In a special case where a polymer was found to contain 5.25 per cent soluble soap, calculated as sodium stearate, the iodine value of the acetone-extracted residue was found to be 345.1. When the acetone-extracted polymer was refluxed with a mixture of 2 volumes of benzene and 1 of alcohol for 1 hour to remove this soap, the iodine value of the polymer increased to 350.6. This is a lower value than expected, which can be accounted for only on the bases that the soap acids were unsaturated.

The presence of soap lowers the carbon-hydrogen ratio, resulting in calculated styrene contents which are too low. Consequently the calculated per cent of theoretical unsaturation is too low. The presence of soap and other impurities reduces the iodine value, which also results in a lower calculated theoretical unsaturation.

When the styrene content is calculated from the iodine value, as shown in Table III, the presence of impurities giving a low iodine value results in a calculated styrene content which is too high. This method for obtaining the styrene content also gives too high results if the butadiene present does not have theoretical unsaturation. If care is taken to remove the soap, the iodine value method should prove to be a fairly accurate procedure for determining the styrene content of commercial GR-S.

IODINE VALUE OF BUTADIENE–ACRYLIC NITRILE POLYMERS

The effect of different reaction conditions on the iodine value of butadiene-acrylic nitrile copolymer is shown in Table VI. These data show that either of two procedures is satisfactory. In one procedure, the polymer can be passed 60 times through a tight mill-roll, and rendered soluble in chloroform, thereby avoiding the use of *p*-dichlorobenzene. However, to save time, a lesser amount

TABLE VII

ANALYSES OF BUTADIENE-ACRYLIC NITRILE POLYMERS

	Polymers	
	Regular nitrile content	High nitrile content
Carbon (per cent)	81.53	79.80
Hydrogen (per cent)	9.53	8.90
C/H ratio	8.55	8.97
Butadiene content from C/H (A) (per cent)	79.2	66.5
Nitrogen (per cent)	6.54	10.19
Acrylic nitrile (per cent)	24.8	38.5
Butadiene from N (B) (per cent)	75.2	61.5
Iodine value	302.2	266
Theoretical iodine value from A (per cent)	81.0	85.0
Theoretical iodine value from B (per cent)	86.0	92.3
Average per cent theoretical iodine value from A and B	83.5	88.6

of milling, together with the use of *p*-dichlorobenzene, will be found advantageous. In either case the use of Wijs solution is preferred, along with addition of 50 cc. of chloroform to the *p*-dichlorobenzene solution. The polar nature of the glacial acetic acid increases the solubility of the polymer and its iodine chloride addition product.

The results of chemical analysis and iodine value of these polymers are given in Table VII, with butadiene contents calculated from both carbon-hydrogen ratios and nitrogen contents. The loss in unsaturation on polymerization is higher than in the case of the butadiene-styrene polymers. This is reflected also in the low plasticity and difficulty in processing the nitrile copolymers, since cross-linking or cyclization reactions during polymerization would be expected to result in loss of unsaturation and decreased processibility.

IODINE VALUE OF POLYCHLOROPRENE

Tests made on Neoprene-GN, using the present method, showed that in 2 hours at room temperature the reaction had proceeded to 56.9 per cent completion (iodine value 169.1) and to 64.6 per cent (iodine value 191.9) after a 24-hour reaction period. The theoretical iodine value for polychloroprene is 297.1. As no difficulties were experienced in the procedure, it is concluded that the chlorine atom attached to the carbon atom in the second position in

TABLE VIII

IODINE NUMBER AND ISOPRENE CONTENT OF BUTYL RUBBER AND POLYISOBUTYLENE UNDER VARIOUS EXPERIMENTAL CONDITIONS

Polymer	Solvents used	Iodine chloride solution used, Wijs (cc.)	Reaction period (hours)	Reaction temp. (° C)	Iodine value	Unsaturation[a] (%)
Butyl B-1.45	100 cc. of $CHCl_3$	20	0.5	24	5.37	1.44
		20	1	24	6.00	1.61
		20	4	24	7.10	1.90
		10	0.5	24	4.90	1.31
		10	1	24	5.49	1.47
		10	4	24	6.65	1.78
		5	0.5	24	4.13	1.11
		5	1	24	4.50	1.21
		5	4	24	5.62	1.51
		2	0.5	24	3.22	0.86
		2	1	24	3.22	0.86
		2	4	24	3.48	0.93
		10	0.5	3	3.87	1.04
		10	1	3	4.24	1.14
		10	4	3	4.88	1.31
		5	0.5	3	3.36	0.90
		5	1	3	3.44	0.92
		5	4	3	3.86	1.04
		3	0.5	3	3.29	0.88
		3	1	3	3.32	0.89
		3	4	3	3.49	0.94
		2	0.5	3	3.17	0.85
		2	1	3	3.22	0.86
		2	4	3	3.17	0.85
Polyisobutylene (30,000 molecular weight)		20	1	24	1.37	0.37
		10	1	3	1.37	0.37
		2	0.5	3	1.39	0.37
		2	1	3	1.37	0.37
		2	4	3	1.39	0.37
	50 grams of $C_6H_4Cl_2$ +50 cc. of $CHCl_3$	5	0.25	3	1.09	0.30
		5	1	3	1.15	0.31
		5	2	3	1.36	0.36
		5	3	3	1.36	0.36
Butyl X		5	0.25	3	3.00	0.81
		5	1	3	3.20	0.86
		5	2	3	3.32	0.89
		5	3	3	3.32	0.89
Butyl X-1		5	0.25	3	4.58	1.23
		5	1	3	5.16	1.38
		5	2	3	5.36	1.44
		5	3	3	5.46	1.46
Butyl X-2		5	0.25	3	6.50	1.74
		5	1	3	7.35	1.97
		5	2	3	7.80	2.09
		5	3	3	7.91	2.12

[a] $\text{Unsaturation} = \frac{\text{iodine number of polymer} \times 100}{372.8}$.

the butadiene base unit offers hindrance to the iodine chloride addition reaction. This was previously noted[6], when it was found that addition of iodine chloride by the Kemp-Wijs method took place to the extent of only 30 per cent. A comparison of these results also shows the greater activity of the iodine chloride in carbon tetrachloride. Another experiment, employing the present

TABLE IX

ANALYSIS OF NATURAL AND GR S VULCANIZATES
Rubber Tread Compositions[a]

	I	II	III
GR S (21% styrene)	100.00	50.00	25.00
Smoked sheets	...	50.00	75.00
Stearic acid	3.00	3.00	3.00
Kosmobile 77	45.00	45.00	45.00
Zinc oxide	5.00	5.00	5.00
Sulfur	3.00	3.00	3.00
Santocure	1.25	1.25	1.25
El. Sixty	0.50	0.50	0.50
Total	157.75	157.75	157.75
Calculated Rubber Contents			
Natural rubber, per cent	0.00	31.8	47.6
Natural rubber hydrocarbon (% natural rubber × 0.95), per cent	0.00	30.2	45.2
GR S rubber, per cent	63.4	31.7	15.8
GR S rubber hydrocarbon (% GR S × 0.925), per cent	58.7	29.3	14.7
Chemical Analysis			
Acetone extract, per cent	7.8	5.6	4.0
Chloroform extract, per cent	2.0	1.0	0.75
Sulfur, combined, per cent	1.27	1.86	2.13
Iodine value	225.1	232.6	235.2
Natural R. H. (chromic acid method), per cent	1.45	31.3	45.3
Natural rubber, per cent	1.53	33.0	47.6
GR S hydrocarbon, per cent	58.8	29.0	15.9
GR S rubber (GR S hydrocarbon ÷ 0.93), per cent	63.1	31.2	17.1

$$\% \text{ GR S hydrocarbon} = \frac{A(100\text{-}B) - 372.8\,C}{D} \times 100$$

A = iodine value of extracted vulcanizate
B = combined per cent acetone and chloroform extracts
C = per cent natural rubber hydrocarbon. Determined by chromic acid method
D = iodine value of extracted GR S. Average for 13 lots GR S rubber = 347.0

[a] Vulcanized 20 minutes at 142° C.

procedure using 0.05 gram of Neoprene and a 24-hour reaction period at room temperature, resulted in forcing the addition to 67.3 per cent, corresponding to an iodine value of 199.9.

IODINE VALUE OF BUTYL RUBBER

The present method, or the Kemp-Wijs procedure, was found not to be applicable to Butyl rubber, since substitution occurs so readily in both procedures as to introduce large uncertainties in the low unsaturation values. Various procedures have been studied (Table VIII).

Samples of 0.5 gram were used in all cases. In the case of chloroform only as the solvent, it required overnight to dissolve the Butyl rubber. When hot *p*-dichlorobenzene was employed, as in the case of the butadiene polymers, the solution time ranged from 20 to 30 minutes. The concentration of sodium thiosulfate solution was reduced to 0.05 *N* to increase the accuracy of the titration. In other respects the procedure was the same as previously outlined.

The best choice of analytical procedure appears to be to employ 50 grams of *p*-dichlorobenzene and 50 cc. of chloroform as solvent to obtain maximum speed. The use of 5 cc. of Wijs solution and carrying out the reaction for 2 hours in the dark at ice-water temperature appear to keep substitution at a minimum, and at the same time complete the addition reaction with a series of Butyl rubbers of varying unsaturation.

It is seen that a sample of polyisobutylene having an average molecular weight of about 30,000 has an iodine value of 1.36, corresponding to an unsaturation of 0.36 per cent. If this unsaturation arises from free end valences, the unsaturation of the Butyl rubber arising from the addition of the diolefin should be corrected by subtracting this value. On the other hand, polyisobutylene may contain some diolefin.

Hanus solution and iodine chloride in carbon tetrachloride were tried, but were found to be more reactive than Wijs solution, causing considerable substitution. In the case of a 1.45 Butyl rubber, the iodine values at room temperature and 1-hour reaction period in the dark were: Hanus, 6.86; iodine chloride in carbon tetrachloride, 6.57; and Wijs, 4.25.

ESTIMATION OF NATURAL AND SYNTHETIC RUBBER IN MIXED VULCANIZATES

The chromic acid oxidation method of Kheraskova and Korsunskaya[7] which was improved by Burger, Donaldson, and Baty[8] serves to determine the natural rubber content of a mixture of GR-S and natural rubber. This method, however, does not give the combined amount of natural rubber and GR-S in an unknown vulcanized mixture. For this purpose the authors have applied the present method to finely divided samples, which were first acetone- and chloroform-extracted in the regular manner.

The composition tested was a tread formula given in Table IX. The results of analysis presented in this table appear to be satisfactory.

DUPLICABILITY OF METHOD

The duplicability of the present iodine chloride method is indicated by Table X, which shows that the present procedure applied either to crepe or butadiene-styrene copolymers is probably duplicable within ±0.25 per cent. Care must be taken, however, to guard against nonhomogeneity in the samples. Errors in sample weight should be kept within ±0.0001 gram and the titration within ±0.03 cc. Since the end-point in the titration is sensitive to 0.01 cc., it is not difficult to duplicate results within the above limits.

Substitution takes place more readily with the new method than with the Kemp-Wijs procedure, owing to the greater chemical activity of the iodine chloride in carbon tetrachloride compared with the Wijs reagent. By limiting the time of reaction to 1 hour, the error due to substitution is very small and, judged from the results on crepe rubber, the addition reaction appears to be completed in this time.

TABLE X

IODINE VALUE OF CREPE AND BUTADIENE-STYRENE COPOLYMER RUBBER UNDER VARIOUS CONDITIONS

Polymer	Method	Reaction time (hours)	Reaction temp. (° C)	Iodine value	Difference (%)
A	Present	1	24	356.1	0.34
		1	24	357.3	
B	Present	1	24	312.7	0.49
				314.2	
C	Present	1	24	296.6	0.27
				297.4	
Crepe rubber	Present	1	24	352.3	0.09
Crepe rubber[a]	Present	1	24	352.0	
Crepe rubber	Present	16	24	373.0	
Crepe rubber[a]	Kemp-Wijs	2	3	352.5	
Crepe rubber[a]	Kemp-Wijs	1	24	353.9	

[a] 12 passes through tight mill rolls.

CONCLUSION

The procedures outlined in this paper make it possible to determine accurately the unsaturation of a wide range of synthetic rubberlike substances prepared by the polymerization of monoölefins and diolefins.

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HEAT GENERATION IN FLEXED RUBBER *

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The problem of heat generation in tires assumes new importance with the advent of synthetic rubber and the increased use of reclaimed rubber. Even if reduced speeds may prevent heat blowouts, higher temperatures mean that both fabric and rubber are operating under unfavorable conditions. Synthetic rubber, in particular, is then working at reduced tensile strength and tear resistance. It is more susceptible to heat embrittlement, cuts, and abrasion.

A number of flexometers for rubber testing have been described[1], and some of these instruments have been widely used[2]. The flexometer described here is characterized by simplicity of construction, high speed, and convenience of operation.

FLEXOMETER DESIGN

Figure 1 is a drawing of the flexometer. Sixty-cycle current from a 12-volt filament transformer, the primary of which is controlled by a variable transformer, is supplied to a coil in a radial magnetic field so that the coil and the

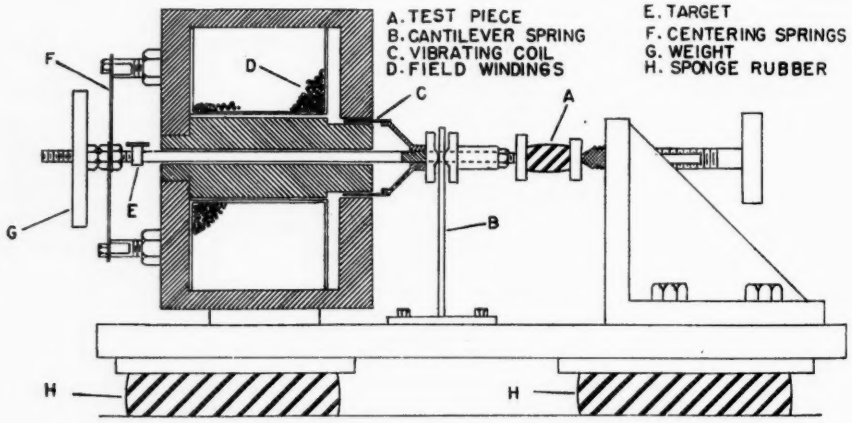

FIG. 1.—Drawing of flexometer.

system to which it is attached vibrate with this frequency. The coil has an inside diameter of 3 inches, and consists of two layers of No. 18 enameled copper wire wound on a thin fiber tube, twenty-three turns in each layer. The current through the coil is usually about 5 amperes, but it may be as high as 15 amperes. The magnetic field is produced by a field coil operated from the 110-volt direct current line and is about 8000 gauss. Figure 2 shows the

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static force calibration curve for the system. Figure 3 is a photograph of the instrument.

Since the central system of rod, coil, cantilever spring, and rubber test-piece is driven at a frequency of 60 cycles per second, it is advantageous to have the natural frequency of the system somewhere near this value. For this adjustment, weights can be added or removed from the end of the rod. In practice, it is necessary only to change this adjustment for stocks of an extreme range of stiffness.

The cantilever spring is a ¼-inch gage stainless steel plate, 3 inches wide and 7¼ inches long. The cantilever spring has proved to be durable, but it limits the amplitude which can be used by its action, when deflected, of disturbing the centering of the coil. A coil spring would not have this disadvantage and is designed into a later model now under construction.

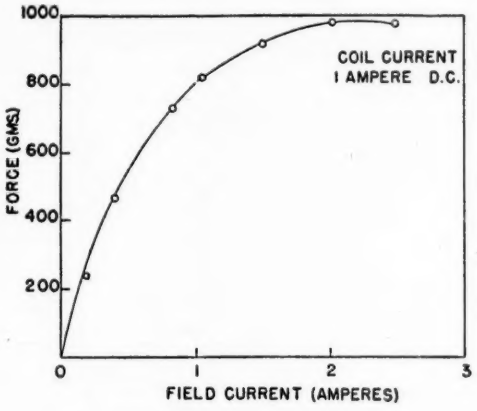

FIG. 2.—Force calibration curve.

The impedance of the system is rather complicated. The electrical impedance of the coil at rest must be combined with the mechanical impedance to secure the over-all impedance. Morse[3] gives the equations for a loud-speaker which can be used for the present case.

The mechanical impedance of the system with c.g.s. units assumed is:

$$Z = \sqrt{R^2 + \left(2\pi\nu M - \frac{K}{2\pi\nu}\right)^2} \qquad (1)$$

where R = constant of proportionality between frictional force and velocity
M = mass
K = spring constant or force per unit displacement
ν = frequency

The force on the coil is proportional to the instantaneous current through it so that

$$F = DI \qquad (2)$$

where F = force in dynes
I = current in amperes
D = constant of proportionality

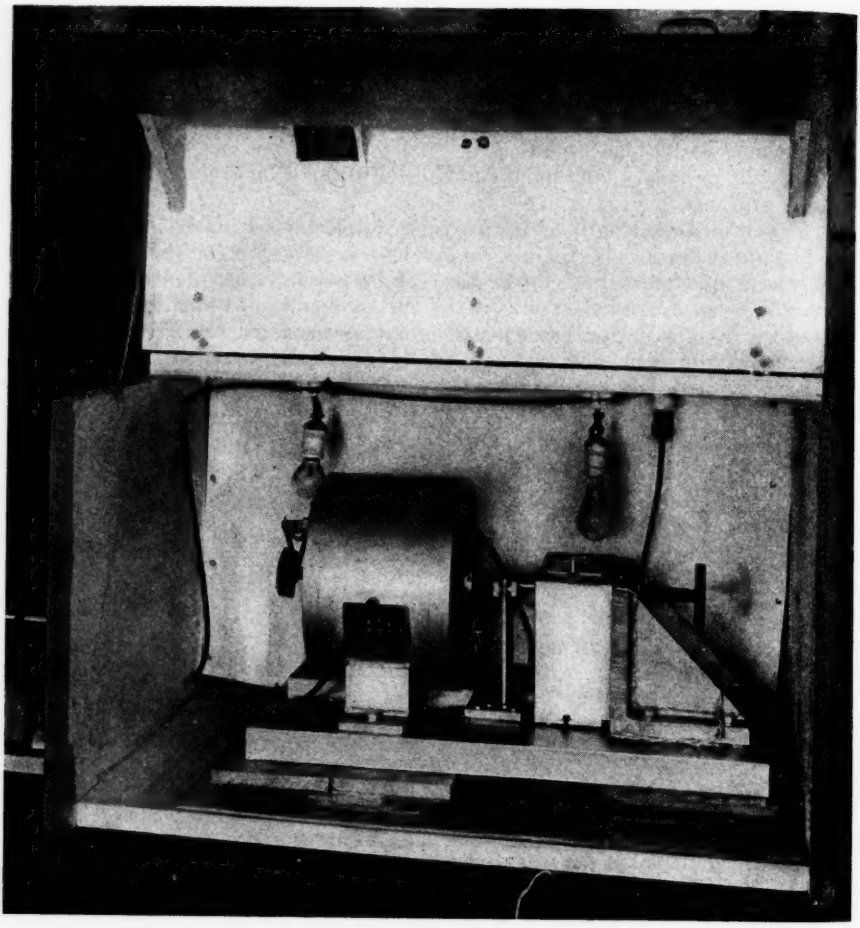

FIG. 3.—Photograph of flexometer.

The total impedance of the coil is given by:

$$Z_E = \left\{\left[R_c + \frac{GR}{Z^2}\right]^2 + \left[2\pi\nu L_c + \frac{KG}{2\pi\nu Z^2} - \frac{2\pi\nu MG}{Z^2}\right]^2\right\}^{1/2} \qquad (3)$$

where R_c = resistance of coil
$G = D^2 \times 10^{-7}$
L_c = self-induction of coil

The amplitude of the motion for an applied alternating voltage of maximum value E is:

$$A = \frac{DE}{2\pi\nu Z Z_E} \qquad (4)$$

Some of the values for the system can be given. The d.c. resistance of the coil is 0.26 ohm. Its self-induction, L_c, is 217 microhenrys; hence its static

impedance at 60 cycles is 0.27 ohm. From Figure 2, D can be determined as 931,000 and G as 8.67×10^4. The constants for the mechanical system will depend on the rubber test-piece. Under suitable operating conditions, the impedance measured when running with a gum stock was 0.35 ohm and for a GR-S tread stock, 0.75 ohm. As the test-piece heats up, the impedance changes somewhat, and an adjustment must be made in the coil current to maintain a constant amplitude. But the system is stable and tends to settle down rapidly to a constant amplitude.

The impedance of the coil, when the flexometer is running, can readily be determined by measuring the voltage and current. It is possible that some technique might be worked out to use this measurement in the evaluation of the stiffness or damping of the rubber, but the relations appeared to be so involved that no attempt was made to do this.

TESTING PROCEDURE

The rubber test-piece is a rectangular block 2 inches long with a 1-inch square base. It is the same test-piece used for the Goodyear pendulum rebound test. It is mounted between metal plates containing recessed fiber inserts. The test-piece is put under a static compression of 6 per cent. This is determined by a spacer block. Figure 4 shows that the observed temperature rise is rather insensitive to this compression.

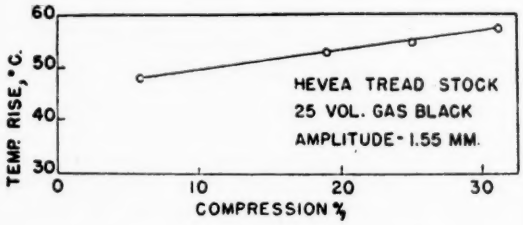

FIG. 4.—Temperature rise *vs.* static compression.

The temperature in the middle of the block is measured by a needle thermocouple and a Leeds & Northrup temperature indicator. The needle thermocouple was made by running a silk-insulated constantan wire through a hypodermic needle and soldering the wire to the needle at the point.

The temperature of the block is measured at the start of the test and after running for 10 minutes at a fixed amplitude. The difference in these readings and the calibration of the thermocouple determine the temperature rise due to flexing. Figure 5 shows that after 10 minutes the temperature of the test-piece approximates the equilibrium temperature. The test-piece is enclosed in a jacket during the test, the temperature of which is controlled at 35° C. A small fan is provided to circulate the air.

The amplitude is determined by the visual observation of a suitable target through a magnifying lens. The target consists of a solid black arrowhead pointing at a broad black line on a white background. In vibration the arrowhead and the line are spread out or blurred, due to the persistence of vision. The current through the coil is set so that the point of the blurred arrow just touches the edge of the blurred line. The amplitude is then one-half of the

distance between the arrowhead and the edge of the line when at rest. For different amplitudes one target can be readily replaced by another.

The mixtures here reported were accelerated with mercaptobenzothiazole in conventional formulas published previously[4].

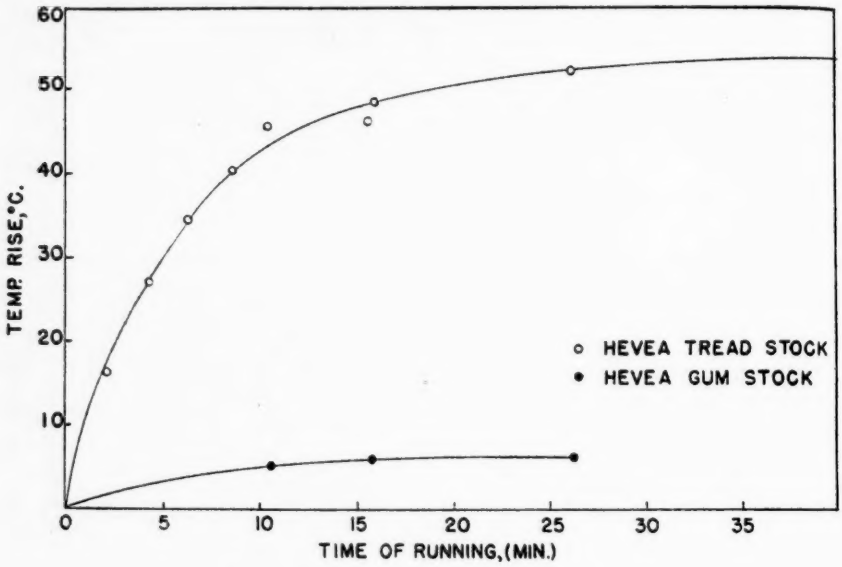

FIG. 5.—Dependence of temperature rise on time.

Figure 6 shows the cooling curve for a test-piece mounted in the flexometer; the temperatures had been determined for various elapsed times with the needle thermocouple. The rate of cooling at the start is about 7° C per minute, which corresponds to the cooling rate to be expected while a reading is being taken after a test-piece is run. As the reading is obtained within about 10 seconds after stopping, the technique seems accurate enough in this respect for the comparison of rubber mixtures. Insertion of the needle at the end of the test, without stopping the flexometer, also gives accurate results.

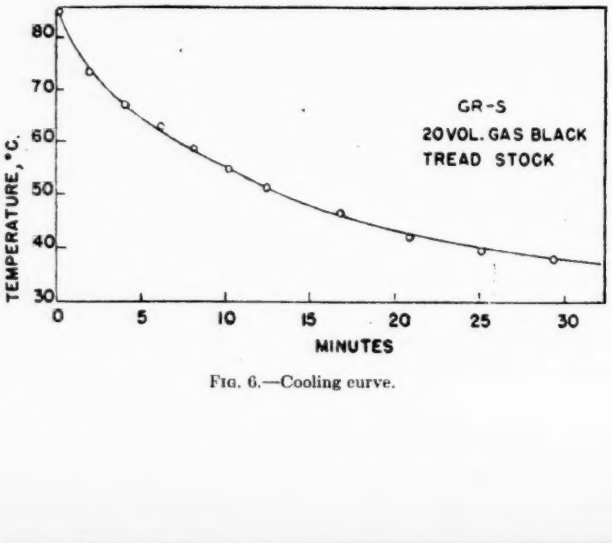

FIG. 6.—Cooling curve.

Figure 7 illustrates the temperature gradient along the test-piece after running. The maximum temperature occurs in the mid-plane of the test-piece, where the alternating strain is greatest and the heat losses are a minimum. The curve shows some advantage in the technique of measuring the temperature of the test-piece in the middle rather than at the end, even if this

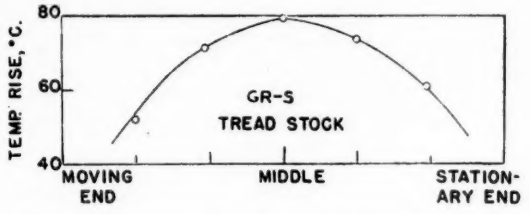

FIG. 7.—Temperature gradient along test piece after running.

precludes the possibility of a continuous temperature record. It is noteworthy that the temperature at the moving end is somewhat lower than that at the stationary end, probably due to a fanning action of the air on the moving end.

Figure 8 shows the effect of amplitude of vibration on heat generation. Theoretically the heat generation increases with the square of the amplitude; but, as the temperature rises, the resilience increases, the modulus decreases, and the heat losses increase so that actually the relation between heat generation and amplitude is approximately linear.

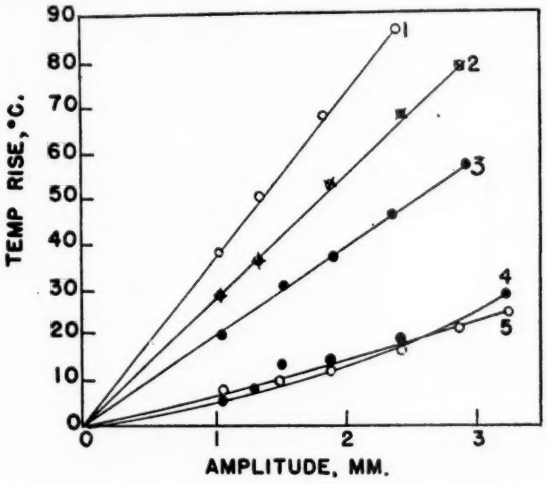

FIG. 8.—Effect of amplitude on heat generation. 1, GR-S, 20 volumes gas black; 2, Hevea, 25 volumes gas black; 3, Hevea, 20 volumes gas black; 4, Hevea, 20 volumes zinc oxide; 5, Hevea, 20 volumes thermatomic black.

Figure 9 gives some curves relating the observed temperature rise to various pigment loadings in mercaptobenzothiazole-accelerated stocks. The higher heat generation in GR-S compared to natural rubber is emphasized.

Figure 10 illustrates the effect of the initial uniform temperature of the test-piece on the ensuing temperature rise. The jacket temperature was

adjusted to be equal to the initial temperature in each case. When a test-piece is run in the flexometer, the final temperature reached represents an equilibrium value between heat generation and heat losses. These curves show that the rate of heat generation is not constant but falls off at the higher ambient temperatures so equilibrium is reached sooner and with a lower temperature rise than would otherwise be the case.

The data in Figure 11 bring out the facts that the temperature rise for GR-S is relatively independent of cure in the technically useful range, and that the sensitivity of the equipment for differentiating between small variations in heat generation is best at higher amplitudes. Figure 12 represents a further study of the effect of cure on heat generation for both natural rubber and GR-S tread stocks.

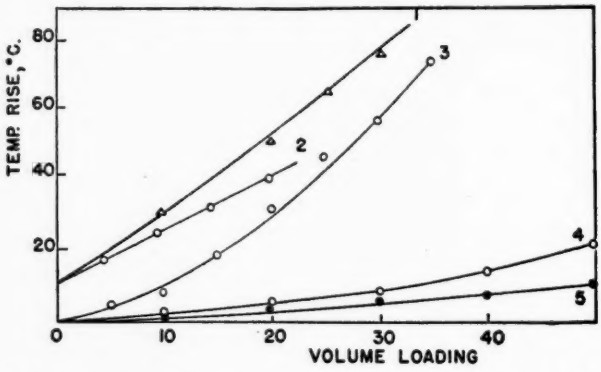

FIG. 9.—Effect of pigment loading on heat generation at amplitude of 1.55 mm. 1, Wyex-GR-S; 2, zinc oxide-GR-S; 3, gas black-Hevea; 4, zinc oxide-Hevea; 5, thermatomic-Hevea.

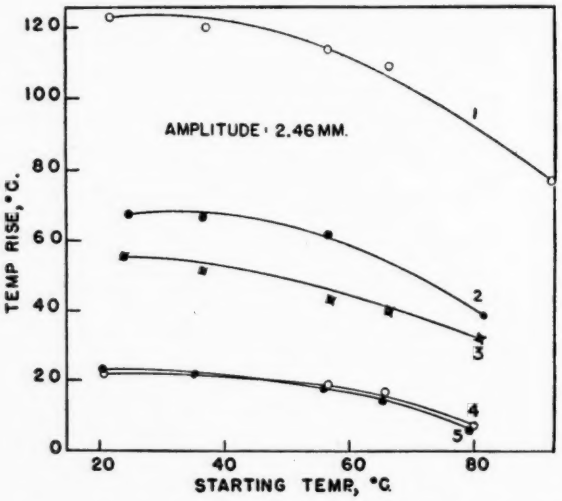

FIG. 10.—Effect of temperature on heat generation at amplitude of 2.46 mm. 1, GR-S-25 volumes gas black; 2, Hevea-25 volumes gas black; 3, GR-S-20 volumes zinc oxide; 4, Hevea-20 volumes zinc oxide; 5, Hevea-20 volumes thermatomic black.

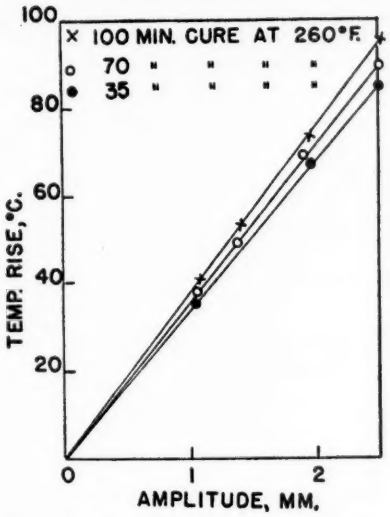

FIG. 11.—Effect of amplitude and cure on heat generation of GR-S-20 volumes gas black.

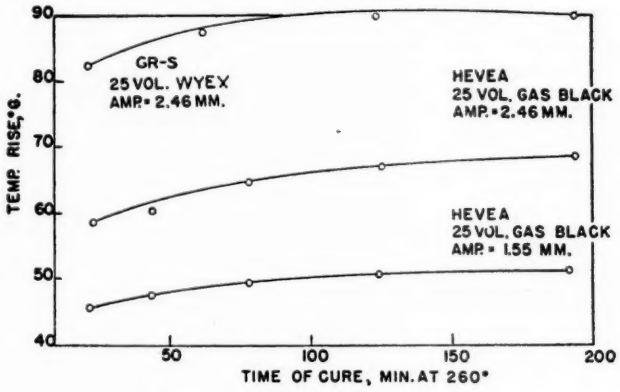

FIG. 12.—Effect of cure on temperature rise.

FLEXOMETER RESULTS

Although from a practical standpoint these flexometer measurements are comparatively straightforward, the measured temperature rise actually represents a composite result from many interrelated factors, the ultimate analysis of which would go back to the molecular structure of the rubber. For many purposes it is sufficient for a better understanding of the results to consider the vibration properties of the rubber as determined by suitable vibration tests[5].

The small effect of cure on temperature rise (Figures 11 and 12) results from the fact that for these stocks both modulus and resilience increase with cure and have opposite effects on the heat generation at constant amplitude. Figure 13 shows the course of the curves from the vibration test. Calculated

relative values of heat generation at constant amplitude, H_x, show a slight rise with increasing cure, such as was actually observed with the flexometer. For comparison at constant force, the increase in modulus and resilience with cure would both tend to reduce the heat generation. Consequently there is a large drop in H_f, the calculated relative heat generation for cycles of constant force, as the cure progresses.

Similarly, the course of modulus and resilience curves with temperature[6] anticipate the results shown in Figure 10.

In any given comparison in this work, all of the rubber compounds were flexed at the same amplitude. It is well recognized that conditions of deformation in a pneumatic tire tread are complicated and cannot be simulated exactly

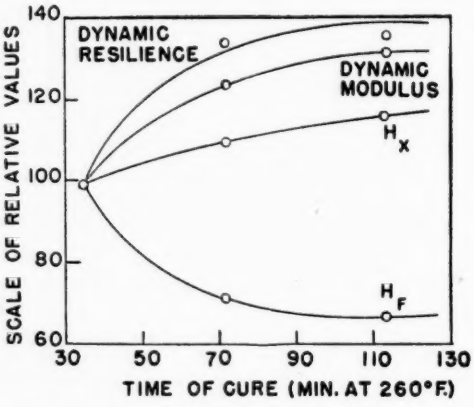

FIG. 13.—Effect of cure on vibration properties of GR-S tread stock.

by a constant amplitude comparison. In a general way, bending of the tread due to the tire deflection is an amplitude cycle relatively independent of the stiffness of the stock. On the other hand, the pressure between the rubber and the road brings into play a force cycle, for which the deformation will vary inversely with the stiffness of the stock. For the correct interpretation of the flexometer results, it is important to know the relative proportion of the heat generation which occurs under these two conditions. A resiliometer test was run to secure some information on this point and to try to separate the two effects.

Two tread stocks of WPB qualities A and C were compared in a tire test on the resiliometer. For brevity the stocks will be referred to as tread stocks A and C, respectively. The results here given were obtained for a 9.00 × 20 tire with a Goodyear All-Weather tread design. The tire had a two-way tread, half the circumference being of stock A, the other half of stock C. It was run at a speed of 30 miles per hour on a resiliometer, the wheel of which was 7 feet in diameter. Temperature measurements after running were made at tread shoulder and tread center by a needle thermocouple. The needle was inserted to a depth of 0.54 inch at the shoulder and 0.43 inch at the tread center.

The tire was run at a series of inflation pressures but at a constant deflection of 1.12 inches. This procedure had the effect of maintaining essentially con-

stant the deformations which could be considered as strictly amplitude cycles; the deformations which should be regarded as force cycles varied with the inflation pressure. The results of the test are shown in Figure 14, where the temperature rise is plotted against the inflation pressure. Smooth curves were obtained which have definite intercepts on the temperature rise axis. For the tread center, for both stocks, this intercept is about 40 per cent of the temperature rise at 65 pounds per square inch inflation, the normal inflation pressure. For the shoulder the intercept is about 60 per cent of the total rise. Presumably the intercept represents the temperature rise that can be attributed

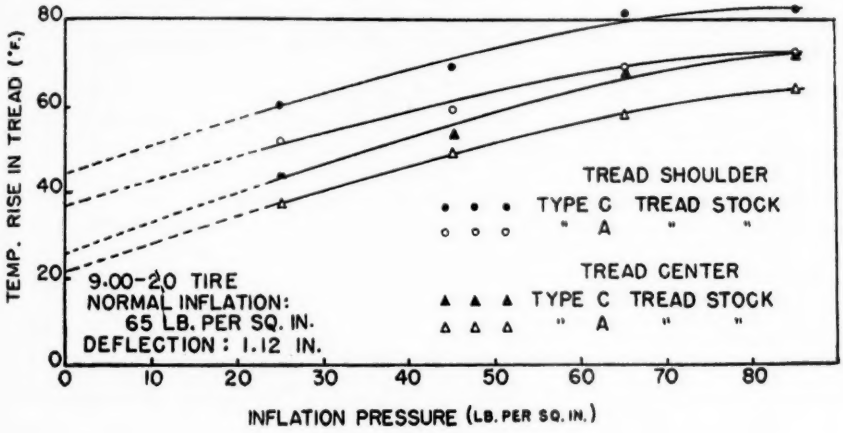

Fig. 14.—Resiliometer results.

to amplitude cycles which are independent of the inflation pressure. The deformations involved are controlled by the change in shape of the deflected carcass and are independent of the stiffness of the stock. The above analysis is an "averaging type" with obvious limitations in precision. The effect on the tread temperature of the heat developed in the carcass is assumed to be negligible. In spite of these limitations, it is felt that the experiment gives a picture of the mechanism of heat generation in tire treads which is essentially correct.

The average ratio of the temperature rise for stock C to that for stock A in the resiliometer test was 1.17. A flexometer comparison of the stocks showed a ratio of 1.27. In general, flexometer comparisons at cycles of the same amplitude can be expected to rate stocks in the correct order for tire tread temperature rise, but to exaggerate the differences between the stocks, because about half of the tread temperature rise occurs under conditions corresponding to constant force cycles. This same tendency is shown in results of an experiment reported by Mackey, Anderson, and Gardner[7], in which two stocks containing different amounts of carbon black were compared. Flexometer tests at the same amplitude showed temperature rises of 110° and 92° F for the high-black and low-black stocks, respectively. In a resiliometer test, tread temperatures of 146° and 140° F, respectively, were observed.

As long as this characteristic of the flexometer results is kept in mind, it is not a serious disadvantage for laboratory testing, since it tends to emphasize trends and differences. For a more precise evaluation of the heat generation

of rubber compounds in tire treads, more attention should be given to some means of also taking into account the heat generation of the stocks under cycles of the same force. For solid tires the constant force comparison would have much more significance than the constant amplitude comparison.

If it is desired to compare rubber stocks when subjected to cycles of the same force, it is necessary to determine the dynamic moduli of the compounds by an independent test[4] and then to run them in the flexometer at amplitudes which are inversely proportional to the moduli. Alternatively, use may be made of the linear relation between amplitude and temperature rise (Figure 8) to correct observed temperature rises to values which are inversely proportional to the moduli. One of the difficulties with such procedures is that the variation of modulus with temperature is not taken into account.

The inherent advantage of a flexometer type of test to measurements at room temperature, or even at the same elevated temperature, is that it compares stocks operating, not at the same temperature, but at different temperatures built up by flexing. It is possible that a flexometer comparison of rubber stocks can be devised which will simulate more closely conditions in a tire tread than anything yet reported. It seems worth while to suggest that, in a flexometer of the type described, the test-piece could be loaded against a dynamometer, the relatively small vibrations of which would be proportional to the alternating force. By suitable magnification of the motion of the dynamometer, the force amplitude could be observed and set at a constant value for a series of stocks. The average rating from the constant force and constant amplitude comparison should then give a precise rating of the stocks in respect to their heat generation as tire treads.

RELATION OF HEAT GENERATION TO RUBBER STRUCTURE

The transformation of mechanical energy into heat, which occurs in the flexing of rubber, is naturally thought of as due to (1) some process similar to the frictional development of heat during the flow of a viscous liquid, or (2) solid friction such as is responsible for vibration damping for metals and other solids. A dilute solution of rubber in an organic solvent approximates a pure liquid in viscous behavior. As the concentration is increased, the phenomena become more complicated and the flow properties depend on the rate of shear. This is due to the interaction of the dissolved molecules or a tendency to assume equilibrium positions with respect to one another. In other words, it represents the appearance of a rudimentary type of elasticity. Such systems are called elasto-viscous. In the case of rubber, the elastic nature of the solution becomes more and more pronounced as the concentration is increased; correspondingly, the viscous nature is suppressed. Consequently, raw rubber may be thought of as being at the end of such an elasto-viscous system. Vulcanization further enhances the elastic character at the expense of the plastic or viscous nature. But it is not unexpected that both aspects of the structure should be evident in the heat generation phenomena.

It is customary to think of elasto-viscous systems in terms of mechanical models[9]. The mechanical model for an elasto-viscous material represents the elastic and viscous elements as a spring connected in series with a piston which moves in a viscous liquid. Equations for such a system were first provided by Maxwell's relaxation theory. Since that time considerable work has been published on such systems, both from the experimental and theoretical side. Reasonable success has been achieved in explaining the general pattern of the

phenomenon, but quantitative discrepancies are usually found. The limitations of the theories are well recognized and the more powerful concepts of modern theories of flow[10] might well be applied to this problem. The results with rubber vibrations should furnish a good experimental background for extension of the theory.

The quantity η which has been used in previous publications[11] to denote the internal friction for rubber vibrations has usually been called the "equivalent viscosity"[12]. It is not the same, by definition, as the coefficient of viscosity of a liquid. It is the frictional stress per unit of strain velocity. But it has the same dimensions as the coefficient of viscosity and can be thought of as arising from gradients of shear velocity. Its similarity to an ordinary viscosity coefficient will be emphasized in the following discussion.

Philippoff[13], making use of the theories of Hencky and Weissenberg and the Maxwell model, introduced a quantity called the "dynamic viscosity", η', to show the effect of frequency. He deduced the relationship:

$$\eta' = \frac{\eta_0}{1 + (\omega\tau_0)^2} \tag{5}$$

where η_0 = viscosity for small stresses
ω = $2\pi \times$ frequency
τ_0 = time constant of relaxation = time required for an applied stress to drop to the fraction $1/e$ of its value

τ_0 gives the order of magnitude of the time required for flow to develop. It is equal to the ratio η_0/S_0, where S_0 is the modulus of rigidity.

It can be shown that the internal friction, η, for rubber follows essentially this same frequency dependence and thus simulates the functional dependence of the viscosity of elasto-viscous systems on the frequency. Equation 5 shows a falling off of η' as the frequency increases. A transition between elastic and viscous behavior occurs when $\omega\tau_0$ approaches unity.

Figure 15 illustrates how equations of the type of Equation 5 can be fitted to experimental data of Stambaugh for rubber[6]. The points represent the experimental data; the curves are plots of the following equations:

For GR-S tread stock:

$$\eta = \frac{1.67 \times 10^5}{1 + (0.0036\,\omega)^2} \tag{6}$$

For *Hevea* tread stock at 110° C:

$$\eta = \frac{1.4 \times 10^5}{1 + (0.0097\,\omega)^2} \tag{7}$$

For *Hevea* tread stock at room temperature:

$$\eta = \frac{7.4 \times 10^4}{1 + (0.0034\,\omega)^2} \tag{8}$$

Aside from the formal difference between η and η', it is doubtful whether much significance can be given to τ_0 as a relaxation time. It has been generally realized that a single relaxation time is inadequate to describe the elasto-viscous nature of rubber. Although the equation should be used with much caution in this respect to secure insight into the structure of rubber, it does serve to classify the friction-frequency phenomena for rubber vibrations as

being elasto-viscous in nature; and the load is alternately supported by elastic and viscous elements of the structure. The molecular equilibrium positions when under stress are evidently always somewhat displaced with reference to the unstressed equilibrium positions. There is not only an accommodation to

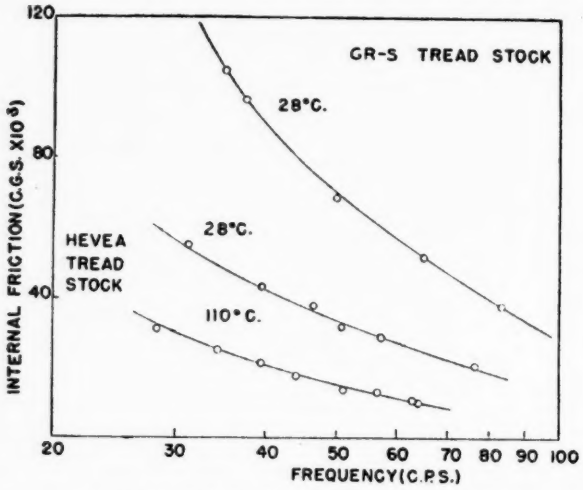

FIG. 15.—Dependence of internal friction on frequency.

the stress by displacement about the unstressed equilibrium positions, but also a rearrangement of the equilibrium positions which requires time. Furthermore, the range of mechanical vibrations appears to be in the transition region where $\omega\tau_0$ approaches unity.

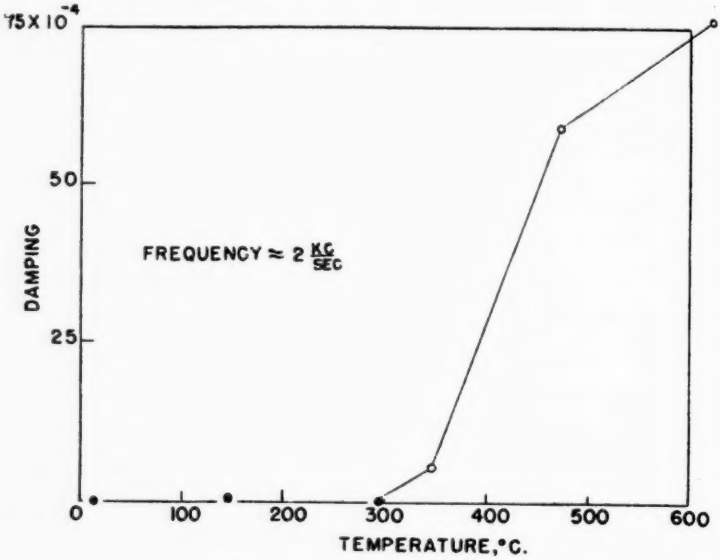

FIG. 16.—Damping for aluminum[14].

The dependence of the internal friction for rubber on temperature is more illuminating in regard to structure. It can be shown that this dependence is abnormal in comparison to that of metals and most other solids. Figure 16 gives a curve for the damping for aluminum at various temperatures as determined by Förster and Köster[14]. Here damping means the logarithmic decrement or the logarithm of the ratio of the amplitudes of two successive free vibrations. The rise in the damping curve with increase in temperature is characteristic of metal, glass, most plastics, and similar materials. With rubber, on the other hand, the resilience improves at higher temperatures.

Figure 17 shows the specific loss for Lucite as a function of temperature, as measured by Rinehart[15]. The specific loss is the loss of energy per cycle expressed as a fraction of the total vibrational energy. The specific loss is twice the logarithmic decrement.

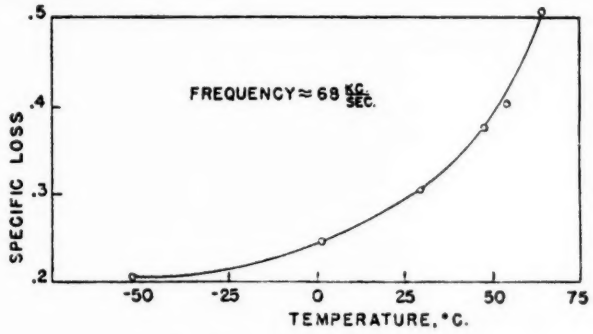

FIG. 17.—Specific loss in lucite[15].

The scale of the curves for aluminum and Lucite shows that the energy loss for the metal is of a smaller order of magnitude, but for Lucite it is the same order of magnitude as that encountered with rubber vibrations. The rise of the curve at higher temperatures for these materials is generally ascribed to increased plasticity.

The fact that the losses for rubber decrease with rise of temperature emphasizes the fact that they probably occur in a structure which is more nearly similar to that of liquids than to that of most solids. The decrease of internal friction for rubber at higher temperatures is not only analogous to the decrease in viscosity which occurs for liquids, but actually shows the same functional relation[6].

Figure 18 is a plot of $\log_e \eta$ against the reciprocal of absolute temperature. For a liquid which does not undergo any structural change in the temperature range, such a plot for viscosity gives a straight line (or at least a good approximation). Thus, the plot indicates a change in structure for GR-S rubber which occurs at about ordinary room temperatures. For natural rubber, on the other hand, this transition point is at a lower temperature[6]. The temperature at which this change of structure occurs appears to be insensitive to cure in the technical range and, as shown, is also relatively insensitive to pigment loading. It is therefore reasonable to suppose that this change of structure is associated with localized and intimate molecular groupings rather than with a larger network structure.

Activation energies can be calculated from the equation:

$$\eta = Ae^{E_0/RT} \tag{9}$$

They have the same magnitude as do activation energies of organic liquid viscosities. For octane the value is 2.18[16]. The values follow:

	E_0, kg.-cal./mole	
	Low temp.	High temp.
Hevea tread stock	7.10	2.06
GR-S tread stock	5.80	2.43
GR-S gum stock	4.83	0.36

The picture obtained from this experimental evidence and line of thinking is that heat generation in flexed rubber arises from the disturbance of equilib-

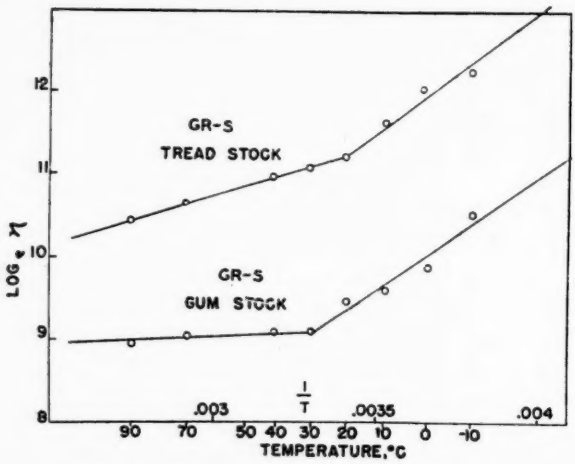

FIG. 18.—Temperature-internal friction relation.

rium molecular configurations. The stress increases the molecular disorder, and when new equilibrium configurations are established, some of the work done appears as heat.

What effect various molecular structures in polymers might have on the internal friction is a complicated question. In the first place, the constitution of the monomers should probably be considered. A great deal of work has been done on the effect of constitution on the viscosity of liquids[16]. Some generalizations have been reached, but they are not satisfactory, and certainly nothing appears from them which could be carried over directly to polymer structure. Nissan, Clark, and Nash[17] made a thorough study of the effect of constitution on the viscosity of liquids. By relating the viscosities to the ratio of the absolute temperature of measurement and the boiling point, they were led to the conclusion that the molecular shape was the chief variable affecting their curves. Dipole moments and the nature of the atoms of the molecule were found to be relatively immaterial compared to the shape of the equipotential surfaces surrounding the molecule. A spheroidal shape gave the highest viscosity for a given temperature ratio.

It seems doubtful that the shape of the monomer molecule could be of compelling influence on the internal friction of a polymer. The chain shape and

structure should be more important, particularly the size and shape of the chain segments which act as kinetic units and serve to build up a structure with configurational energy. The chain length and extent of cross linkages are other features which enter into the picture although their influence may be rather indirect.

Just what characteristic of the molecular structure of synthetic rubber is responsible for its higher heat generation is difficult to say. The low resilience of all synthetic rubbers to date compared to natural rubber leads us to look for the explanation in unique characteristics of the natural rubber structure rather than in specific features of the molecular structure of any one synthetic rubber. In the natural rubber structure we feel reasonably certain of such characteristics as long linear molecules of *cis* form, regular in structure and with the property of aligning themselves readily in the direction of stress. It is well known that the viscosity of elasto-viscous systems decreases with increasing stress, in correlation with the orientation of the structure in the direction of flow. Similarly with natural rubber, this "streamlining" of the long molecules in the direction of stress may be one of the most important reasons for low heat generation. But until more is known of the molecular configurations existing in materials with rubberlike elasticity, such conclusions are only reasonable speculations.

ACKNOWLEDGMENT

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BRITTLE POINTS OF NATURAL AND SYNTHETIC RUBBER STOCKS *

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Because of the present interest in the cold resistance of natural and synthetic rubber vulcanizates, data are presented here which may help compounders to select the correct synthetic rubber for specific applications.

A comparatively simple apparatus for determining the brittle points of plastic and elastic materials was developed by Selker, Winspear, and Kemp of the Bell Telephone Laboratories[1]. While determining the suitability of this apparatus for specification tests, the authors had occasion to determine the brittle points of similar vulcanizates prepared from *Hevea* rubber, guayule rubber, and a wide variety of synthetic rubbers. A description of this apparatus (including the modifications in the original design made by the authors), the recipes of the stocks tested, and the brittle points of the stocks are given here. In addition, a test for brittle point under less severe bending stress is described, and data obtained by this test are included for some of the same stocks.

SIGNIFICANCE OF BRITTLE POINT

The word "brittle" means "easily broken". Kemp, Malm, and Winspear[2] showed that the ease with which natural and synthetic vulcanizates can be broken by bending depends, not only on the temperature, but also on the rate and radius of bending. Increasing the rate or decreasing the radius of bending enhances the possibility of breakage at a given temperature. In other words, rubber vulcanizates behave at low temperatures like so-called plastics at normal temperatures.

To compare vulcanizates from the standpoint of brittleness, it is necessary to define at least two of these variables, and use the third as a criterion of brittleness. For example, the temperature and the rate of bending may be maintained constant in all determinations, and the radius of bending required to fracture the specimens may be considered a measure of brittleness. However, for convenience in measurement and because of closer agreement with many service conditions, the brittle point is generally defined as the temperature at which fracture occurs, assuming that the rate and radius of bending have been established. This is the case with the experiments reported here.

TESTING METHOD

Brittle point apparatus.—The apparatus was constructed essentially as described by Selker, Winspear, and Kemp[1]. It consisted of an insulated steel tank, 18 × 2 × 8 inches. Seven inches from one end on the top was mounted

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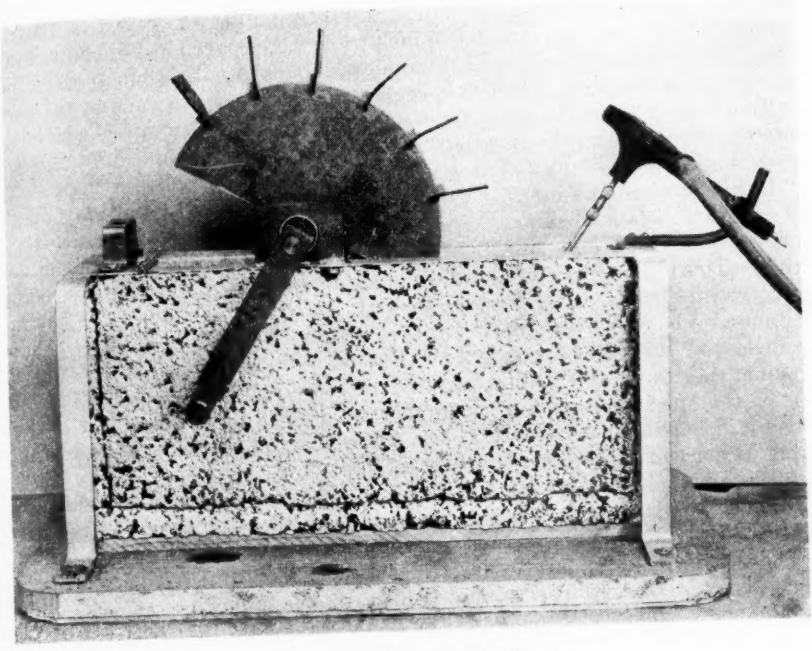

FIG. 1.—Brittle point apparatus.

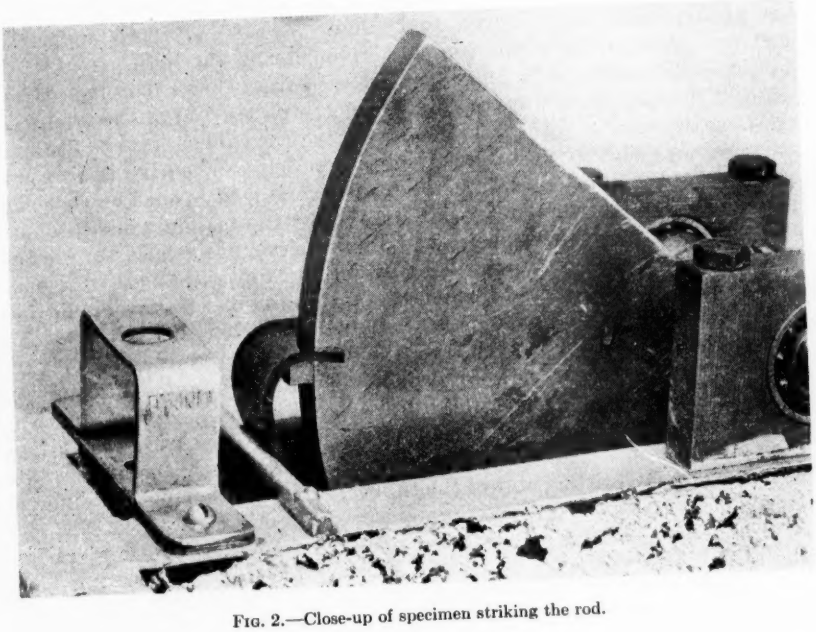

FIG. 2.—Close-up of specimen striking the rod.

a brass semicircle, 4.87 inches in radius and 0.50 inch thick, keyed to a shaft. Six notches, 0.25 inch deep and 0.075 inch wide, were spaced at 2-inch intervals on the rim of the semicircle. Each notch was backed with a block extending 0.25 inch above the rim. A stiff ¼-inch round rod was fixed across the tank exactly 0.5 inch from the rim of the semicircle. The shaft upon which the sample-holding fixture was mounted had a crank which, on rotation, immersed the specimens in the tank. The shaft was supported on ball bearings.

Methyl alcohol was used as the immersion medium and solid carbon dioxide as the cooling medium. The alcohol was circulated by an air-driven stirring motor. The temperature of the alcohol was determined with a thermocouple. The temperature of the alcohol was raised rapidly when desired by adding warm alcohol or inserting a 500-watt immersion heater in the bath.

Photographs of the apparatus appear in Figures 1 and 2. Figure 1 shows the insulated tank, the brass semicircle with six specimens in position for breaking, the crank, and the air-operated stirring motor. Figure 2, a close-up view of the specimen striking the round rod, shows the support for a thermometer although, as mentioned above, the authors preferred to use a thermocouple for measuring the temperature of the alcohol.

A close-fitting sheet metal hood was placed over most of the tank after insertion of the specimen to prevent splashing of the alcohol when the crank was turned rapidly. This hood is not shown in the photographs.

The brittle point apparatus used in these tests deviated from the design proposed by Selker, Winspear and Kemp in the following respects. The insulated steel tank was 4 inches longer to accommodate the air stirrer. Ball bearings were used on the crankshaft to reduce rotational friction and thus obtain a greater velocity of impact. A ¼-inch round rod mounted across the tank was used instead of an arm mounted in the side of the tank because the former arrangement was believed to be more stable and reproducible. A bracket was provided for supporting a thermometer in the bath.

Testing.—Specimens, 1 × 2 inches, were died from sheets 0.08 inch thick. One end of the specimens was inserted in a notch on the rim of the semicircle by grasping the corners with pliers and stretching the rubber so as to decrease its thickness and allow it to slip freely into the notch. When the tension was relaxed, the rubber fit snugly in the notch and overlapped ¼ inch on each side of the semicircle. It was found advisable to insert and test only one specimen at a time on the rim of the semicircle to obtain maximum velocity of impact.

The tank was filled to within 3 inches of the top with methyl alcohol, which was cooled to the desired temperature by chunks of solid carbon dioxide. The cooled alcohol was circulated by the stirring device. When the alcohol had arrived at the desired temperature, the semicircle was turned so that the specimen was immersed in the cold alcohol. Exactly 2 minutes after immersion of the specimen, the crank was turned rapidly in a clockwise direction so that the specimen struck the horizontal bar just as it rose from the alcohol. The temperature at which the specimen was cracked by this treatment was considered to be the brittle point of the rubber. The brittle points of different specimens of the same stock generally agreed within 0.5° F.

Rubbers tested.—Similar stocks were prepared from the following rubbers for the brittle point tests:

Natural: smoked sheet, deresinated guayule (2.7 per cent acetone-extractable remaining).

Chloroprene polymers and copolymers: Neoprene-E, Neoprene-FR, Neoprene-GN, Neoprene-ILS.

Butadiene-styrene copolymers: Buna-S (Naugatuck GR-S), Buton-S (Firestone GR-S), Chemigum-IV (Goodyear GR-S), Hycar-OS-10 (styrene content higher than GR-S), Hycar-OS-20 (stearic acid content lower than GR-S).

Buna-N type copolymers: Butaprene-NXM, Butaprene-NM, Butaprene-NX, Chemigum-I, Chemigum-X, Hycar-OR-15, Hycar-OR-25, German Perbunan, Stanco Perbunan, Thiokol-RD.

TABLE I

COMPOSITION, CURE, AND PROPERTIES OF VULCANIZATES FROM NATURAL RUBBERS AND BUTADIENE-STYRENE COPOLYMERS

	Smoked sheet	Deresinated guayule	Buna-S	Buton-S	Chemigum-IV	Hycar-OS-10	Hycar-OS-20
Composition							
Smoked sheet	100.0	...	...	...	...	...	...
Deresinated guayule	...	100.0	...	...	...	...	...
Buna-S	...	...	100.0	...	...	...	...
Butaprene-S	...	...	...	100.0	...	...	...
Chemigum-IV	...	...	...	...	100.0	...	...
Hycar-OS-10	...	...	...	...	...	100.0	...
Hycar-OS-20	...	...	...	...	...	...	100.0
Semireinforcing carbon black	75.0	75.0	75.0	75.0	75.0	75.0	75.0
Zinc oxide	5.0	5.0	5.0	5.0	5.0	5.0	5.0
Stearic acid	2.0	2.0	...	...	...	...	...
Phenyl-α-naphthylamine	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Dibenzothiazyl disulfide	0.8	0.8	...	...	...	...	...
Zinc dimethyldithiocarbamate	0.1	0.1	...	...	...	...	...
Tetramethylthiuram monosulfide	...	...	0.5	0.5	0.5	0.5	0.5
Sulfur	2.5	2.5	2.0	2.0	2.0	2.0	2.0
Cure							
Temperature (° F)	260	260	287	287	287	287	287
Time (minutes)	20	25	20	20	20	20	20
Tensile strength (lbs. per sq. in.)	2840	2010	1890	1790	2100	2090	2060
Ultimate elongation (percentage)	450	360	230	220	320	240	310
Shore hardness (after 10 sec.)	68	72	67	70	62	69	61
Brittle point (° F)	−71	−56.5	−68	−56	−71	−4.5	−63

TABLE II

COMPOSITION, CURE, AND PROPERTIES OF VULCANIZATES FROM CHLOROPRENE AND ISOBUTYLENE POLYMERS AND COPOLYMERS

	Neoprene E	Neoprene FR	Neoprene GN	Neoprene ILS	Vistanex medium	Buty B
Composition						
Neoprene-E	100.0	...	...	...	...	...
Neoprene-FR	...	100.0	...	...	...	...
Neoprene-GN	...	...	100.0	...	...	...
Neoprene-ILS	...	...	...	100.0	...	...
Vistanex (medium)	...	...	...	...	50.0	...
Smoked sheet	...	...	...	...	50.0	...
Butyl-B	...	...	...	...	...	100.0
Semireinforcing carbon black	75.0	75.0	75.0	75.0	75.0	75.0
Zinc oxide	10.0	...	5.0	10.0	5.0	5.0
Light-calcined magnesia	10.0	...	4.0	10.0	...	...
Litharge	...	10.0	...	...	...	...
Stearic acid	0.5	1.0	0.5	0.5	2.0	1.5
Wood rosin	5.0	...	...	...	...	...
Di-o-tolylguanidine salt of dicatechol borate	...	...	...	1.0	...	...
Phenyl-α-naphthylamine	2.0	2.0	2.0	2.0	...	...
Dibenzothiazyl disulfide	...	...	...	...	0.8	...
Mercaptobenzothiazole	...	...	...	...	...	0.5
Zinc dimethyldithiocarbamate	...	...	...	...	0.1	...
Tetramethylthiuram disulfide	...	...	...	...	...	1.0
Sulfur	1.0	1.0	...	...	2.0	1.5
Cure						
Temperature (° F)	307	287	287	307	287	307
Time (minutes)	40	40	40	40	20	90
Tensile strength (lbs. per sq. in.)	2250	2420	2550	2590	1300	1290
Ultimate elongation (percentage)	210	190	260	160	390	650
Shore hardness (after 10 sec.)	75	73	81	86	55	62
Brittle point (° F)	−29	−41	−31	+22.5	−57	−33

TABLE III

COMPOSITION, CURE, AND PROPERTIES OF VULCANIZATES FROM BUNA-N TYPE COPOLYMERS

Composition	Chemigum-I	Chemigum-X	Hycar-OR-15	Hycar-OR-25	German Perbunan	Stanco Perbunan
Chemigum-I	100.0	...	...	...	...	...
Chemigum-X	...	100.0	...	...	...	...
Hycar-OR-15	...	...	100.0	...	...	...
Hycar-OR-25	...	...	...	100.0	...	...
German Perbunan	...	...	...	...	100.0	...
Stanco Perbunan	...	...	...	...	...	100.0
Semireinforcing carbon black	75.0	75.0	75.0	75.0	75.0	75.0
Zinc oxide	5.0	5.0	5.0	5.0	5.0	5.0
Stearic acid	1.0	1.0	1.0	1.0	1.0	1.0
Phenyl-α-naphthylamine	1.0	1.0	1.0	1.0	1.0	1.0
Dibenzothiazyl disulfide	1.75	1.75	1.75	1.75	1.75	1.75
Sulfur	1.75	1.75	1.75	1.75	1.75	1.75
Cure						
Temperature (° F)	274	274	274	274	274	274
Time (minutes)	60	60	60	60	60	60
Tensile strength (lbs. per sq. in.)	2790	2850	2630	2560	3040	2540
Ultimate elongation (percentage)	230	150	290	310	300	300
Shore hardness (after 10 sec.)	76	84	72	70	73	70
Brittle point (° F)	−11	+36.5	+5	−18	−35.5	−29

TABLE IV

COMPOSITION, CURE, AND PROPERTIES OF VULCANIZATES FROM ORGANIC POLYSULFIDES AND BUNA-N TYPE COPOLYMERS

Composition	Thiokol-F	Thiokol-FA	Thiokol-RD	Butaprene-NXM	Butaprene-NM	Butaprene-NX
Thiokol-F	100.0	...	...	...	...	...
Thiokol-FA	...	100.0	...	...	...	...
Thiokol-RD	...	...	100.0	...	...	...
Butaprene-NXM	...	...	...	100.0	...	...
Butaprene-NM	...	...	...	...	100.0	...
Butaprene-NX	...	...	...	...	...	100.0
Semireinforcing carbon black	75.0	75.0	75.0	75.0	75.0	75.0
Zinc oxide	10.0	10.0	5.0	5.0	5.0	5.0
Stearic acid	0.5	0.5	1.0	1.0	1.0	1.0
Phenyl-α-naphthylamine	...	...	1.0	1.0	1.0	1.0
Dibenzothiazyl disulfide	0.35	0.3	1.75	1.75	1.75	1.75
Diphenylguanidine	0.1	0.1	...	...	...	...
Sulfur	...	...	1.75	1.75	1.75	1.75
Cure						
Temperature (° F)	298	298	274	274	274	274
Time (minutes)	50	40	60	60	60	60
Tensile strength (lbs. per sq. in.)	1490	1390	2260	2370	2160	2950
Ultimate elongation (percentage)	240	190	170	320	260	230
Shore hardness (after 10 sec.)	82	81	87	71	69	75
Brittle point (° F)	−19	−26	+50	+1	−31	−3.5

Isobutylene polymer: Vistanex Medium (blended 50-50 with smoked sheet so as to vulcanize).

Isobutylene copolymer: Butyl-B.

Organic polysulfides: Thiokol-F, Thiokol-FA.

Results.—The formulas, cures, tensile strengths, ultimate elongations, hardnesses, and brittle points of the vulcanizates prepared from the above rubbers are given in Tables I to IV. It is apparent that the GR-S stocks (Table I) were the only synthetic vulcanizates with brittle points as low as the smoked sheet stock. Hycar-OS-10, although a butadiene-styrene copolymer, gave a stock with a much higher brittle point than the GR-S stocks. The guayule stock (Table I) and the Vistanex-smoked sheet blend (Table II) had quite low brittle points, but not so low as the GR-S or smoked sheet stocks. It is interesting to note that the GR-S stocks differed among themselves with respect to brittle point by as much as 15° F.

The brittle points of the Neoprene stocks (Table II) varied widely, depending on the type of Neoprene. The brittle point of the Neoprene-FR stock was fairly low; that of the Neoprene-ILS stock was high.

The stocks prepared from Buna-N type rubbers (Tables III and IV) had brittle points, ranging from a very high value for the Thiokol-RD to a fairly low value for the German Perbunan stock. The Butaprene-NM stock had the lowest brittle point of the domestic Buna-N type stocks.

The stocks prepared from the true Thiokols (Thiokol-F and Thiokol-FA, Table IV) had surprisingly low brittle points, considering the semiplastic nature of these synthetic rubbers.

EFFECT OF ESTER TYPE SOFTENERS

Ester type softeners improve the cold resistance of Hycar-OR-15 and Stanco Perbunan vulcanizates[3]. Ester type softeners are of value also for improving the processing of these synthetic rubbers and all other Buna-N type copolymers. To determine the effect of these softeners on the brittle points of typical Buna-N type stocks, the Thiokol-RD, Hycar-OR-15, Stanco Perbunan, Butaprene-NM, and Chemigum-I stocks were recompounded with 10 parts of dibutyl sebacate, 10 parts of dibutyl phthalate, and 10 parts of diisobutyl adipate. The addition of these softeners made the uncured stocks practical for factory processing. Esterlike softeners have also been shown to improve the cold resistance of Neoprene-FR vulcanizates[4]. Therefore, the Neoprene-FR stock was also recompounded with the same softeners in the same proportions.

The stocks containing the softeners were given the same cure as formerly. The tensile properties, hardnesses, and brittle points are given in Table V.

TABLE V

EFFECT OF ESTER TYPE SOFTENERS ON PHYSICAL PROPERTIES AND BRITTLE POINTS OF VULCANIZATES CONTAINING SOFTENERS

Synthetic rubber type	Tensile strength (lbs. per sq. in.)	Ultimate elongation (percentage)	Shore hardness (after 10 sec.)	Brittle points (° F)		
				With softeners	Without softeners	Lowering due to softeners
Thiokol-RD	2140	300	65	−20	+50	70
Hycar-OR-15	1990	440	55	−41	+ 5	46
Chemigum-I	1900	310	56	−63	−11	52
Stanco Perbunan	1790	470	50	−70	−29	41
Butaprene NM	1710	380	47	−79	−31	48
Neoprene-FR	1470	270	52	−82	−41	41

The data show that the inclusion of the softeners in the recipes resulted in a pronounced drop in the brittle points of the stocks. The Thiokol-RD stock exhibited the greatest lowering in brittle point, but the Butaprene-NM and Neoprene-FR stocks had the lowest brittle points. The softeners likewise had an effect on tensile properties and hardness; the tensile strengths were decreased, the ultimate elongations were increased, and the hardnesses were decreased.

DETERMINATION OF BRITTLE POINTS UNDER LESS SEVERE BENDING STRESS

The foregoing experiments gave data on brittle points when the specimens were subjected to a rapid rate of bending and an acute radius of bending.

The work of Kemp, Malm and Winspear[2] indicates that, when the rate of bending is decreased and the radius of bending is increased, the brittle points of natural and synthetic vulcanizates are lowered. The present authors also have conducted experiments with a low rate and a large radius of bending. These experiments were carried out in a simple fashion, but gave quite consistent results.

The procedure employed was as follows. A strip, 6.0 inches long, 0.25 inch wide, and 0.08 inch thick, was cut from a cured tensile sheet. The strip was clamped at each end to wooden sticks, as shown in Figure 3*A*. The strip

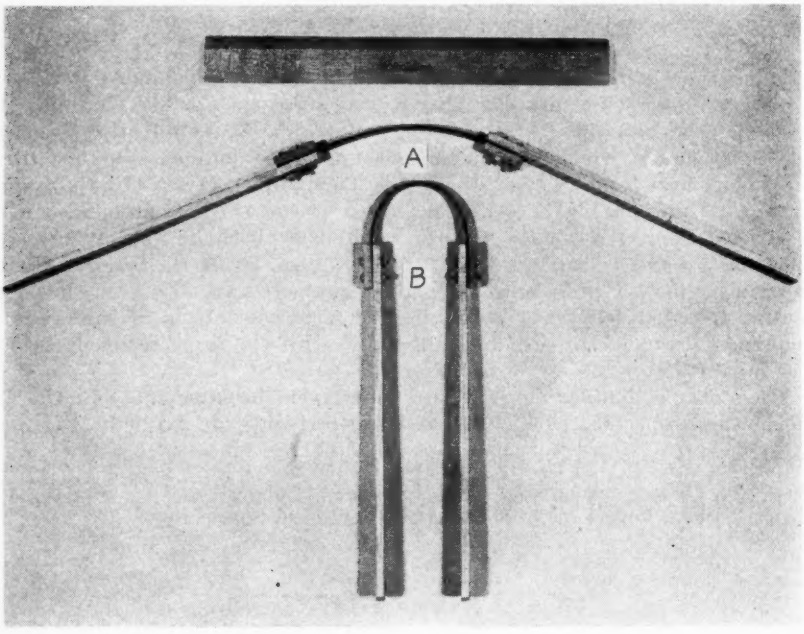

FIG. 3.—Positions of rubber specimen in breaking point test.

was maintained in this slightly bent condition and was immersed in acetone at the test temperature. After 2-minute immersion, the strip was slowly bent while still immersed until the sticks were parallel (Figure 3*B*). If the strip broke during this operation, the temperature of the acetone was raised slightly and the test repeated with a new specimen. The highest temperature at which the strip broke was considered to be the brittle point of the stock. This temperature was found to be the same within 0.5° F for different specimens of the same stock. A Scott T-50 apparatus[5] was used to provide the cold acetone bath for this brittle point test. This apparatus afforded a convenient means of cooling the specimens because of its shallow cooling tray and easy temperature regulation.

The results of these brittle point tests with low rate of bending and large radius of bending are given in Table VI. Included are the corresponding rapid-bend brittle points obtained with the Bell Telephone Laboratories apparatus for comparison. The slow-bend brittle points are 25° to 45° F lower

TABLE VI

COMPARISON OF BRITTLE POINTS DETERMINED WITH RAPID AND WITH SLOW BEND

Vulcanizate	Brittle point (° F)		
	Slow bend	Rapid bend	Difference
Chemigum-IV	< −106.5	−71	35.5
Smoked sheet	− 96.5	−71	25.5
Stanco Perbunan	− 71	−29	42
Neoprene-E	− 64	−29	35
Neoprene-GN	− 60.5	−31	29.5
Hycar-OR-15	− 37.5	+ 5	42.5

than the corresponding rapid-bend brittle points. Of particular interest is the very low brittle point of the Chemigum-IV stock when determined by the slow-bend test; it was below the lowest temperature obtainable in the Scott T-50 apparatus with solid carbon dioxide in acetone as the cooling medium.

CONCLUSION

The slow-bend brittle point test does not have the same practical significance as the Bell Telephone Laboratories brittle point test because most rubber articles which are exposed to low temperatures in service are required to withstand fairly rapid flexing. If the slow-bend brittle point test were used as a criterion of the cold resistance of these rubber articles, it might qualify the rubbers for a lower temperature than they could safely withstand in service. The brittle point test developed by the Bell Telephone Laboratories is simple and sensitive. It is believed that this test may advantageously be used to study all cold resistance problems where damage to the rubber itself and not increase in stiffness is the first consideration.

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BEND-BRITTLE AND SHATTER POINTS OF RUBBERLIKE MATERIALS *

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Within the past two years the performance of rubberlike compositions at low temperatures has become important. A number of tests have been devised to measure the loss of rubberlike properties of many of these compositions.

As the temperature is lowered, the first indication of the loss of rubberlike properties is hardening of the material. As the temperature is lowered further, the material continues to stiffen and harden to a point where it becomes quite inflexible; bending or striking with a solid object then causes breaking or shattering, due to the brittleness of the material. Up to this time the temperature at which breaking occurs has been called the "brittle point" of the material, with no distinction between the temperature at which breaking occurs on bending and the temperature at which breaking occurs on striking with a sharp blow from a solid object. It would be easy to assume that the two points occur at the same temperature.

Koch[1] tested the brittle point of elastic materials by measuring the bend stress with a micrometer gauge placed in the center of the specimen that was supported at each end. By observing the distortion caused by weights, the elastic modulus could be measured to the breaking point, which occurred at a definite temperature. This bend-brittle temperature was called the "high elasticity" temperature by Houwink[2] and the "elasticity" temperature by Whitby[3]. An apparatus was developed by the Thiokol Corporation[4] for determining the flexibility of rubberlike materials at low temperatures. The samples are mounted between two plates and bent by turning a crank. The apparatus was designed so that the distance between the plates can be varied. The temperature of breaking was called the "brittle point".

Kohman and Peek[5] tested the brittle point by bending a strip through 90° with a hammer blow. They found that the brittle temperature was independent of the dimensions and the bending angle; however, a high rate of deformation was necessary for the duplication of results. Kemp[6] applied this test to rubber samples, and likewise made no differentiation between bend-brittle point and shatter point. A similar method[7] was reported from Germany except that, in place of a hammer blow, a falling weight was used to break the sample which was bent back upon itself.

Selker and coworkers[8] mounted their samples on a wheel and, by rotation, caused the samples to strike against a projection on the frame to give a bend test. The rate of bending was not stated; however, a high rate of operation would probably simulate a shatter test. Recently[9] this apparatus was improved to control the rate as well as the magnitude of stress.

Garvey[10] attempted to differentiate between a freezing temperature, a stiffness by bending under a load, and a brittle point. The brittle point was tested by placing a rod on the opposite end of a securely held sample and

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bending the sample by striking the rod with a hammer. The temperature of breaking was the brittle point.

A sample of plasticized polyvinyl chloride was tested at low temperature by Russell[11] for a break after cooling for 5 minutes at each temperature. The point of breaking occurred with no observable bending.

In making a bend test by cooling a sample and bending through an angle, it was noticed that the breaking temperature did not correspond to the shatter point when struck a sharp blow with a hammer, and that in the former case the break was usually a straight fracture, whereas in the latter it was a shattering into a number of pieces. A recheck of the tests showed that shattering occurred at a higher temperature than the bend-breaking point. It was considered advisable to determine whether this condition existed in a large number of elastomers.

DETERMINATION OF POINTS OF CHANGE

Bend-brittle test.—An adaptation of the Hycar brittle test was run by dieing samples from a sheet 0.0625 inch thick to make the samples 3.0 inches long and 0.25 inch wide. Each end of the sample was placed in holes drilled in the test block. The holes were 0.25 inch in diameter and 2.0 inches from center to center. This caused the sample to form an arch approximately 1.25

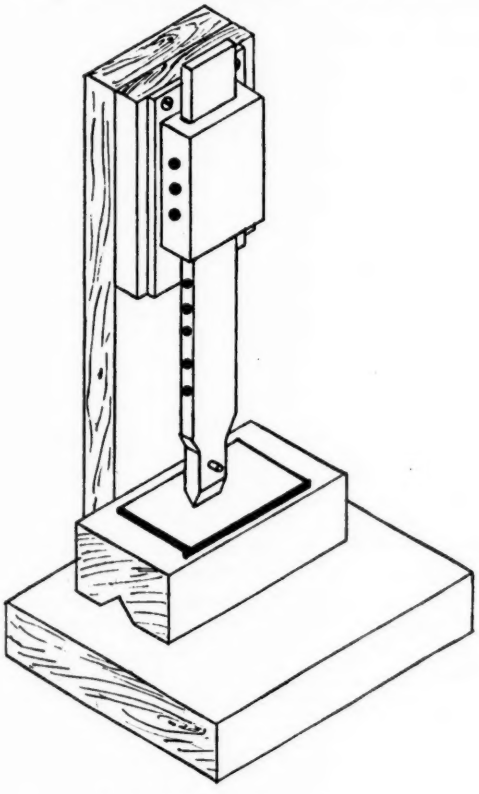

FIG. 1.—Shatter point apparatus.

inches high. The samples are bent by placing a rod on the sample and pushing firmly. The rate is sufficient to bend each sample in 1–1.5 seconds.

Shatter point.—The apparatus (Figure 1) consisted of a steel bar mounted vertically in a sleeve fitted with ball bearings for free sliding. The bar weighed 5 pounds and had a cutting edge at its lower end of a 90° wedge, 0.010 inch wide and 1.0 inch long. For very soft compounds the bar was dropped from a height of 3.0 inches. This distance was sufficient to shatter the sample without cutting it. For samples above 50 Shore hardness, a height of 5.0 inches was used. The base upon which the sample was placed was hardwood.

Hand bend test.—The sample was grasped by gloves kept in the cold box and bent with a continuous motion through 90° at a rate from 1–1.5 seconds. It was found that the hand bend test was practically identical with the bend-brittle test; therefore, the latter was used in place of the hand bend test in the following runs.

The cold box used was described by the du Pont Company[12]. The temperature was lowered in steps of approximately 5° F, and kept at each interval for 15 minutes before testing. After each test, the samples were examined for breaks while still in the cold box.

EFFECT OF VARIABLES

Effect of plasticizers.—To a Neoprene-FR base compound, equal amounts of various plasticizers were added, and the compounds cured. The peak cures, as indicated by tensile, elongation, and hardness, were selected for the test. Table I shows the results of the bend-brittle and shatter points corresponding

TABLE I

EFFECT OF PLASTICIZERS ON BEND-BRITTLE AND SHATTER POINT IN A NEOPRENE FR COMPOUND [a]

Plasticizer (20.5 parts by wt.)	Bend brittle point (° F)	Shatter point (° F)
Butyl cellosolve acetate	−82	−69
Diisobutyl adipate	−90	−62
Dibutyl phthalate	−90	−67
Dibutyl sebacate	−90	−76
Diamyl phthalate	−82	−62
Dicapryl phthalate	−82	−67
Plasticizer-SC	−90	−69
Dispersing oil No. 10	−82	−62
Tributoxyethyl phosphate	−90	−62
TP-10 plasticizer	−74	−49

[a] Base formula: Neoprene-FR 100, stearic acid 1, Flectol-H (antioxidant) 2, sulfur 1, litharge 5, white factice 50, Thermax 100, paraffin 1, zenite 0.5.

to the plasticizers used. In all these compounds, two points were noted that had a difference from 5–18° F. There is an indication that, while some plasticizers act as freeze depressants, others, in spite of their low freezing points, do not depress the shatter point as would be expected. Some plasticizers act as freeze depressants, although their freezing points are higher than the brittle or shatter point of the compound. Usually increasing the proportion of plasticizer lowers the bend-brittle and shatter points. Hardness is not an indication of the bend-brittle or shatter points, and this confirms the results found by others[13]. For example, dibutyl sebacate definitely has the better shatter point; however, diisobutyl adipate has a lower hardness at the breaking temperature.

TABLE II

SYNTHETIC RUBBER FORMULAS

	Neoprene		Hycar			Thiokol		Buna S	Butaprene		Butyl B
	GN*	ILS	OR-15	OS-20	OS-10	RD	FA		NM	NXM	
Synthetic	100.00	100.00	100.00	100.00	100.00	100.00	134.00	100.00	100.00	100.00	100.00
Stearic acid	0.50	0.50	0.50	0.50	0.50	0.50	1.00	0.50	0.50	0.50	0.50
Zinc oxide	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00
Sulfur	...	1.50	1.50	1.50	1.50	1.50	1.25	1.25	1.25	1.25	2.00
P-33 black	80.00	80.00	80.00	80.00	80.00	80.00	80.00	80.00	80.00	80.00	80.00
Circo oil	5.00	5.00	5.00	5.00	5.00	5.00	...	5.00	5.00	5.00	5.00
Whiting	9.00	6.50	5.75	5.75	5.25	6.12	6.00	6.00	6.00	6.00	5.80
Paraffin	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
Altax	...	...	1.50	1.50	1.50	1.50	0.50	1.50	1.50	1.50	...
Thionex	...	...	0.25	0.25	0.25	0.25	...	0.25	0.25	0.25	...
DPG	...	...	...	...	...	...	0.13	...	...	...	...
Permalux	...	1.00	...	...	...	...	...	...	...	...	...
Captax	...	...	...	...	...	...	...	...	...	...	1.00
Tuads	...	...	...	...	...	...	...	...	...	...	0.50
Benzoic acid	...	...	...	...	...	...	0.50	...	...	...	...
Cure at 316° F (min.)	20	15	15	15	15	15	20	10	10	10	20
Shore hardness	67	75	70	60	65	85	68	55	60	70	55

Comparison of elastomers.—To determine whether the same phenomenon of shatter point and bend-brittle point existed in materials other than Neoprene, selected mixtures (Table II and III) were tested; the results are shown in Table IV. Two points were observed similar to those found in Neoprene.

TABLE III

POLYVINYL COMPOUNDS TESTED

Polyvinyl chloride-acetate	90.0	...
Calcium stearate	0.9	...
Dibutyl sebacate	37.2	...
Tricresyl phosphate	22.8	...
Polyvinyl butyrate	...	100.0
Calcium silicate	...	100.0
Dibutyl phthalate	...	85.0
Paraffin	...	0.5

TABLE IV

SHATTER AND BEND-BRITTLE POINTS OF ELASTOMERS

	Frozen 15 minutes		Frozen 24 hours	
	Shatter point (° F)	Bend-brittle point (° F)	Shatter point (° F)	Bend-brittle point (° F)
Gum rubber (light load)	−58	−67	...	...
Buna-S	−72	[a]	−60	[a]
Butaprene-NM	−31	−49	−11	−35
Butaprene-NXM	− 3	− 6	...	...
Butyl B-1.5	−49	[b]	−42	[b]
Hycar OR-15	− 3	− 6	...	...
Hycar OS-10	− 6	−13	...	...
Hycar OS-20	−72	[a]	−49	−55
Neoprene-GN	−40	−49	−35	−45
Neoprene-ILS	− 3	−13	...	...
Norepol P-345-D	+10	−13	...	...
Thiokol-FA	−40	−49	−35	−42
Thiokol-RD	+20	+23	...	...
Plasticized polyvinyl chloride-acetate	−58	−67	...	...
Plasticized polyvinyl butyrate	− 4	−49	...	...
Plasticized ethylcellulose	−22	−58	...	...

[a] In good condition at −76° F.
[b] In good condition at −50° F.

The shatter points in all cases occurred at a higher temperature than the bend-brittle point. There is a range between the two points from 3–40° F. Since these stocks do not represent the best cold-resistant mixtures of each type, their properties at low temperatures could definitely be improved by the addition of a freeze-depressant type of plasticizer.

Effect of time of freezing.—Rubber mixtures exposed to low temperature have a higher brittle temperature, due to progressive crystallization. Selected types of synthetics representing the butadiene-styrene, butadiene-acrylonitrile, chloroprene, and polysulfide rubbers were frozen for 24 hours at each temperature (Table IV). Every sample broke at a higher temperature after 24 hours of freezing, and the shatter point was higher than the bend-brittle point. Since the samples were 0.0625 inch thick, it was felt that the shorter time gave a complete quick freeze without complete crystallization, and that the longer

interval indicated a progressive condition if not crystallization. The greatest change, possibly due to crystallization, was found in the Hycar-OS-20 mixture. It is well known that butadiene synthetics do not crystallize easily. However, there are some indications that at very low temperatures crystallization does take place to some extent.

Effect of rate of bending.—For the past two years this laboratory has recognized that the rate of bending varies the bend-brittle temperature. An instantaneous bend point was obtained in the same manner as the bend-brittle point except that the rod was given a hard, sharp push in an attempt to duplicate as rapid a blow as possible; however, the rod was always in contact with the sample. Table V indicates that the instantaneous bend gives a temperature

TABLE V
RATE OF BENDING AND BEND-BRITTLE POINT

	Bend-brittle point (° F)		
	One-sec. bend	Instantaneous bend	Shatter point (° F)
Butaprene NM	−49	−33	−31
Hycar OS-10	−13	− 8	− 6
Neoprene ILS	−13	− 5	− 3
Plasticized polyvinyl chloride-acetate	−67	−62	−58
Plasticized polyvinyl butyrate	−49	− 8	− 4

that approaches the shatter point. If the rate was truly instantaneous, the bend test would be the same as the shatter point. A similar condition was noticed in the hand bend test when the sample was quickly bent back upon itself, in contrast to a slow bend over a 1–1.5 second period. The same conclusions were made by Kemp and coworkers[9] in their studies of the brittle temperature of rubber under variable stress. The shatter point appears to be the true brittle temperature, as the bend test varies with the rate, and approaches the shatter point as the rate of bending increases.

Effect of hardness through fillers.—Harder stocks, as measured with the Shore durometer, appeared to have a more narrow range between the bend-brittle and shatter points, possibly due to lower percentage of rubberlike material in the mixtures, and also to the dilution beyond the reinforcing range which decreases the cohesive bonds. Table VI shows this for three types of

TABLE VI
EFFECT OF LOADING ON HARDNESS IN BEND-BRITTLE AND SHATTER POINT TESTS

	Hardness (Shore A)	Bend-brittle (° F)	Shatter point (° F)
Neoprene-FR	40	−80	−75
	50	−78	−75
	62	−78	−75
	70	−77	−73
	85	−75	−72
Hycar-OR-15	40	−38	−31
	50	−30	−23
	60	−25	−23
	70	−22	−20
Neoprene-GN	40	−50	−39
	50	−48	−38
	60	−45	−36
	70	−42	−34
	80	−36	−33

materials. Each mixture of each type varied only in the semireinforcing carbon black content.

Effect of dropping weight on shatter point.—As mentioned, Kohman and Peek[5] observed that the dimensions of the samples and the bending angle did not affect the brittle temperature, although a high rate of deformation was necessary to duplicate his results. The size of the sample did not seem to affect the bend-brittle or shatter points, except that the dropping weight must be dropped from a height sufficient to produce a sharp blow without cutting the unfrozen sample. This, by experiment, determined the distance through which the weight fell. There is a definite minimum height for various stocks and hardnesses. Trial and error showed that, under 40 hardness in a Shore (Type-A) durometer, a distance of 3.0 inches met these conditions. If the sample gave a shatter affect at a minimum height, dropping the weight through a greater distance did not raise the shatter point. The relation between the thickness of sample and height of dropping was not determined.

There is probably a relation between bend-brittle and shatter points. In most rubberlike materials, a large number of variables would affect the results, such as type of material, loading, softeners, curing agents, and time and temperature of curing or processing. Fuoss[14] found that, in a sample of plasticized polyvinyl compound, there was a change in electrical properties several degrees higher than the brittle point. This electrical point may correspond to the shatter point, which is higher than the bend-brittle point.

In designing specifications for low-temperature testing, it is desirable to state the property or properties to be tested, the time and temperatures of test, the size of specimens, the procedure and apparatus to be used, and the rates of operation of the test.

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EVALUATING LOW-TEMPERATURE STIFFNESS AND BRITTLE POINT IN ELASTOMERS*

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Soft vulcanized natural rubber has the unique property of maintaining excellent flexibility over a wide range of temperatures. This quality has made this material particularly useful in the automotive and aeronautical fields.

Most of the synthetic elastomers in use today are more sensitive to temperature change than is the natural product; accordingly new problems have arisen in compounding for low-temperature service. The various types of elastomers differ in their inherent resistance to stiffening with cold, and the compounding of each type can greatly influence this resistance.

To meet the challenge of these problems, laboratory methods for evaluating low temperature behavior have been set up by many workers. Numerous devices and methods have been developed and, in general, each approach to the study has been the outgrowth of problems in the particular field of the investigator. It is the intention to summarize here, very briefly, some of the more recent work and to present the methods of evaluation employed in these laboratories[1].

Methods for evaluating low-temperature behavior can be divided into two general classifications. In the first are brittle point tests, designed to determine the temperature at which an elastomer has lost its flexibility to the extent that it fractures when subjected to deformation. In the second classification are low-temperature stiffness tests, designed to measure the degree of stiffening that develops in elastomers with drop in temperature and so provide data at temperatures above their brittle points.

The method most applicable to a given low-temperature problem is, of course, predicated on the demands to be made on the product in service. For example, insulated wire for use in high-altitude aircraft must withstand manipulation at very low temperatures. In such an application the insulating material must be designed to resist cracking; consequently a test to study brittle point is indicated. If, however, the function of the elastomer is one of intermittent flexing, as in pump diaphragms, or in deicing boots for airplane wings, it becomes important to design a product which will undergo a minimum of stiffening over the average range of operating temperatures. For this type of study a test of the second classification, a low-temperature stiffness test, is required.

The importance of these two distinct approaches to low-temperature behavior becomes more evident when it is realized that a mixture which has a satisfactorily low brittle point for a given job may not provide a sufficiently low degree of stiffening with drop in temperature, to give the desired flexibility in service.

In the following discussion, brittle point testing and low temperature stiffness testing will be considered independently, since methods for each approach have been set up in these laboratories.

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SUMMARY OF RECENT BRITTLE POINT TESTING

Kohman and Peek[2] described a method whereby a strip of rubber was bent through an arc of 90 degrees by a hammer blow instantly on removal from a refrigerated alcohol bath. They found that, if a high rate of deformation was employed, consistent brittle point data could be obtained which were nearly independent of sample dimensions. The variations in thickness of the samples they tested were in the same order as found in the usual run of laboratory test sheets.

I. G. Farbenindustrie[3] recommended a method in which six samples were tested at one time. Specimens measuring 15 by 60 by 0.5 millimeters were bent double, forming loops, and fastened on a block over which a falling weight was secured. The apparatus was installed in a cooling cabinet, in which temperature control was achieved by blowing air across dry ice. After a suitable conditioning period, the weight was allowed to fall on the looped specimens, and the temperature was noted at which fracturing occurred.

Recently Kemp, Malm, and Winspear[4] extended their commendable work on brittle point testing. They found that the sharply defined brittle point observed when a specimen is bent at high speed through an angle of 90 degrees is lowered when the speed of application or the magnitude of stress is reduced. Their work was carried out using a motor-driven bending device immersed in an acetone bath cooled with dry ice.

Subcommittee V of SAE-ASTM Technical Committee A on Automotive Rubber has recommended the use of a modification of the freeze test of the Thiokol Corporation[5]. This test has been incorporated into a number of recent Aeronautical Material Standards Specifications. The device consists of two parallel plates mounted horizontally, one 2½ inches above the other. The lower plate is stationary, while the upper plate may be raised and lowered by a hand-operated crank. Test pieces 4 inches by 0.25-inch by 0.06-inch are mounted between the plates in loop fashion so that, when the upper plate is lowered, the specimens are bent between the faces of the plates. By changing the stroke of the upper plate, the radius of bending can be varied. A half revolution of the crank produces maximum bending; while full revolutions will flex the piece. The apparatus operates in a cold air cabinet; the cranking mechanism is outside the conditioning chamber. The device is simple and flexible in use, but does depart somewhat from the precision that most recent workers have been endeavoring to bring into low-temperature evaluation.

AMERICAN CYANAMID BRITTLE POINT METHOD

The brittle point tester used in these laboratories has been constructed to bring into one instrument what we have felt to be the salient features of other apparatus developed for this work. Test specimens are 1½-inch strips cut in the mill (grain) direction from regular ASTM test sheets ranging in thickness from 0.070 to 0.085-inch. The standard T-50 test die is a convenient tool for cutting test-pieces, and provides strips 0.10-inch wide. The apparatus has been built to test from six to twelve specimens at one time, depending on the impact strength of the materials in the brittle state.

A bath of denatured alcohol (2B) cooled with dry ice is used for conditioning the samples. This bath has minimum solvent action on natural and synthetic elastomers, and provides a more sensitive, as well as a faster method of conditioning, than is possible with air cooling.

The test-pieces are bent mechanically through an arc of 90 degrees at a reproducible high rate of deformation. When determined in this way, brittle points represent the highest temperature at which fracturing of the elastomer may be expected.

A conditioning period of five minutes has proved sufficient to produce a brittle state at the critical temperature in the natural and the synthetic rubbers tested. In working with new elastomers, however, the effect of time of exposure to cold on the development of brittleness would require investigation.

Apparatus.—A copper tank 5½ by 11 inches is encased in ¾-inch plywood; the latter provides a good degree of insulation for the bath, as well as serving structurally. All mechanical parts are of stainless steel or aluminum to eliminate rusting. Figure 1 shows the tank, with test-pieces (*T*) mounted in the

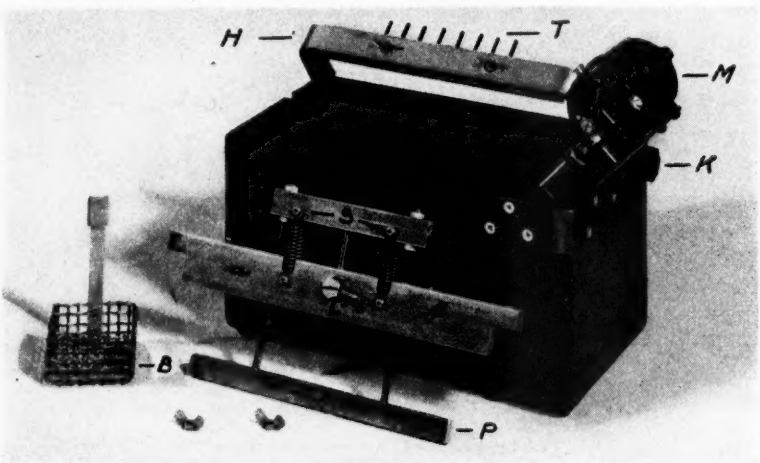

FIG. 1.—Apparatus used for brittle point test.

clamp-type holder (*H*). By turning knob (*K*) counterclockwise, the holder is lowered into the alcohol bath, bringing the test-strips into a horizontal plane. In the foreground is the bending mechanism, consisting of a plunger (*P*) actuated by four springs (*S*). The plunger is "set" by gripping the supporting bar at (*a*) and (*b*) and pressing down on a solid flat surface with sufficient force to stretch the springs ⅝-inch when a spring locking lever (*L*) secures the plunger. In this position, the springs are at a total tension between 95 and 100 pounds. The wire basket (*B*) serves as holder for the dry ice, and is readily lowered into and removed from the bath to provide temperature control to within ±.5° C during the conditioning period. A mechanical stirrer (*M*) assures uniform bath temperature throughout the test.

The assembled apparatus is shown in Figure 2. The test-pieces have been lowered into position, and the plunger has been set and clamped securely into place with wing nuts. In this set up the foot of the plunger is just above the surface of the horizontal test-pieces and is ¼-inch out from the jaws of the holder. Moving lever (*L*) releases the plunger, which travels down in a vertical plane a distance of ⅝-inch, sufficient to bend the test-pieces through an arc of 90 degrees.

Testing procedure.—The tank is filled with alcohol to a depth of about 3½ inches. Test-pieces, in duplicate, are clamped in the holder in convenient order for identification, with about ¾-inch extending. Dry ice is added to the bath, with stirrer running, until the temperature is about 2° C above the highest anticipated for the series of materials to be evaluated. The holder is then lowered into the bath, and the plunger set in place, as in Figure 2. A suitable thermometer is inserted through the side of the tank. Additional dry ice is added, using the wire basket, to bring the temperature down to that

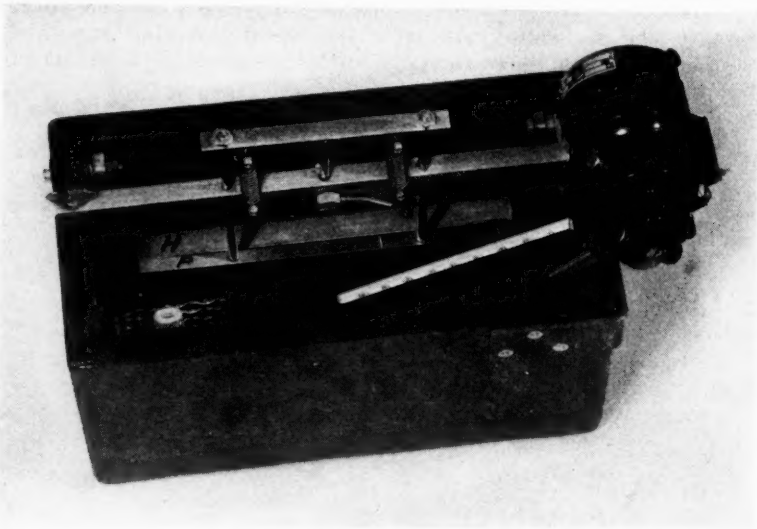

FIG. 2.—Assembled brittle point apparatus.

desired for the first test. After five minutes' conditioning at the test temperature, ±0.5° C, the plunger is released by lever (*L*). The thermometer and plunger mechanism are then removed, and the test-pieces raised out of the bath by knob (*K*) and examined for cracking. Fresh samples of those that have not failed are clamped in place, and the procedure is then repeated at a lower temperature. In our work we usually determine brittle point to the nearest 1° C.

Typical brittle point data obtained with this instrument are given in Table II on four elastomers, compounded as indicated in Table I.

SUMMARY ON LOW TEMPERATURE STIFFNESS TESTING

Although brittle point tests indicate satisfactorily the temperature at which flexibility ceases to exist, they do not provide an insight into the gradual loss of this flexibility with drop in temperature. The need of measuring the effect of temperature on the flexibility of elastomers has been recognized by many workers. Justice could not possibly be done in this short paper to the comprehensive work that has been done by others on this problem. The methods of a few, however, can be mentioned briefly, and our own procedure offered for consideration.

TABLE I

COMPOUND FORMULAE

	Test Stock No.						
	1	2	3	4	5	6	7
Natural rubber	100						
GR-S		100					
Perbunan			100	100	100		
Hycar OR-15						100	100
Channel black	50	50	50	50	50	50	50
Zinc oxide	5.0	5.0	5.0	5.0	5.0	5.0	5.0
Stearic acid	4.0		1.0	1.0	1.0	1.0	1.0
Sulfur	3.0	2.0	2.0	2.0	2.0	1.25	1.25
AgeRite powder	2.0						
M. B. T.	1.0	1.5					
Altax			1.0	1.0	1.0	0.80	0.80
Aero-AC 50						0.15	0.15
Coal-tar softener	5.0	5.0					
Plasticizer A				30		30	
Plasticizer B					30		30
Cure (min.)	30	60	30	30	30	30	30
(temp. ° C)	141	141	141	141	141	153	153

TABLE II

BRITTLE POINT TEMPERATURES

Elastomer	No.	Plasticizer	Brittle temp. (° C)
Natural rubber	1	5% coal-tar softener	−58
GR-S (butadiene styrene)	2	5% coal-tar softener	−69
Perbunan (butadiene-acrylonitrile)	3	None	−50
Perbunan (butadiene-acrylonitrile)	4	30% Plasticizer A	−52
Perbunan (butadiene-acrylonitrile)	5	30% Plasticizer B	−62
Hycar OR-15 (butadiene-acrylonitrile)	6	30% Plasticizer A	−39
Hycar OR-15 (butadiene-acrylonitrile)	7	30% Plasticizer B	−49

McCortney and Hendrick[6], in developing an activating mechanism and diaphragm to be used in Chrysler automatic transmissions, experimented with several tests for comparing the cold resistance of synthetic rubbers. They tried the standard T-50 test and changes in Durometer hardness as a means of determining resistance to cold, but found the results unsatisfactory. A modified T-50 test was then tried in which standard tensile testing dumbbells were stretched to 200 per cent elongation and placed in a room at −40° C. On conditioning, the test-pieces were released, and after 30 seconds the remaining elongation was recorded. The amount the dumbbells failed to return was taken as a measure of low-temperature stiffness. This test also failed to evaluate the qualities desired. After further work McCortney and Hendrick found it necessary to test the diaphragms themselves in the activating mechanism. The test they devised recorded cold resistance in terms of the vacuum, in millimeters of mercury, required to reverse completely the rubber diaphragm. Fortunately in this instance, in the absence of a suitable laboratory test, the mechanism itself was found to be of value in development work.

Clash and Berg[7] developed a low-temperature flexibility test in which the test-specimen was subjected to controlled torsional forces. The apparatus was used in work on the low-temperature behavior of vinyl elastomers. The device employed a rectangular test-specimen mounted with the lower end clamped rigidly, while the upper end was attached to the shaft of a horizontal

pulley to which controlled torque could be applied. The system was set up in a Dewar flask filled, with alcohol to a level above the test-specimen. The bath was refrigerated with dry ice. In this test method, the specimen was subjected to torsional deformation by a constant load at various temperatures. Data on change in flexibility with temperature drop were derived from the angular twist of the test-piece, as observed on the torque head, which was calibrated in degrees of arc.

Koch[8] developed a method which involved measurements of bending stress. In his device, the foot of a micrometer was placed on the center of a small bar test-piece, the ends of which were supported. The set up was mounted in a large test-tube, which in turn was immersed in a Dewar flask containing acetone with dry ice as refrigerant. The test-piece was first frozen to a rigid state, then allowed to warm with the micrometer foot in place under a constant load. As flexibility began to return, the deflection on the micrometer dial was observed. With this device, distortion-temperature curves could be developed and elastic modulus calculated.

AMERICAN CYANAMID LOW-TEMPERATURE STIFFNESS METHOD

The test developed in these laboratories employs tensional forces in a convenient method for low-temperature stiffness comparisons. In all flexing applications elastomers are subjected to stresses of tension, compression, and shear, producing from minute to very appreciable degrees of deformation. Since in most materials moduli in compression and shear are closely related to those in tension, an index of the latter should serve to evaluate the behavior under the complex combination of stresses which occur in flexing.

In rubber terminology the modulus of a compound is the tension, in pounds per square inch of original cross-sectional area, required to produce a specified elongation in per cent. It is, however, usually expressed in pounds per square inch at a particular elongation. Modulus data are commonly used by rubber technologists as indicative of stiffness in rubber compounds.

From the above it becomes apparent that, in studying the effect of temperature drop on the modulus of elastomers, we are not only basing our evaluation on a typical kind of deformation present in flexing, but are also presenting our data in terms at once familiar to rubber technologists.

Our use of stress-temperature data represents a new technique rather than an original approach to the problem. Russell[9] determined stress-temperature relations at 112.5 per cent elongation of polyvinyl chloride compositions as a method for comparing plasticizers for low-temperature service.

In the test to be described, the modulus at 25 per cent elongation is obtained at +25° and at −25° C. The percentage increase in modulus with this drop in temperature is calculated and recorded as the M-25 value of the material tested. The test is carried out on a conventional Scott rubber tensile machine, which may be readily adapted for this work.

The elongation of 25 per cent was selected arbitrarily. In most flexing applications the elongations encountered would be of a low order, and it was felt that 25 per cent was as low as could be conveniently observed on the tensile machine. The temperatures of +25° and −25° C were also chosen arbitrarily to set up a standard test by which many compounds could be evaluated over an average range of operating temperatures. Actually the test is quite flexible. When adapted to a specific problem, compounds could be compared over a

range of temperatures and at an elongation more closely simulating the conditions to be met in service.

In addition to determining the M-25 value in evaluating elastomers, it may be occasionally of interest to take time to determine additional modulus data at intermediate temperatures, and in this way develop modulus-temperature curves. Figure 3 illustrates typical curves prepared from the natural rubber and GR-S stocks described in Table I.

Apparatus.—Tests are run on the Scott rubber tensile machine fitted with a driving pulley to provide a rate of pull of 12 inches per minute. The 50-pound testing range is used for all but extremely stiff stocks.

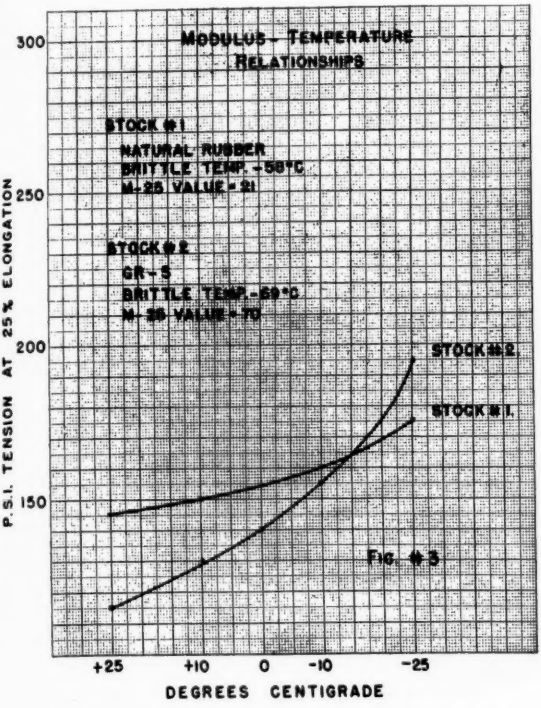

FIG. 3.—Modulus-temperature curves for natural and GR-S rubbers.

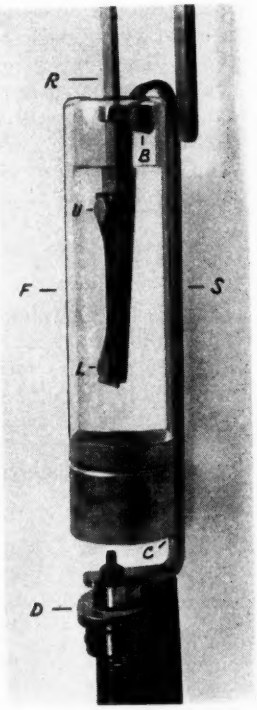

FIG. 4.—Adapter for low-temperature stiffness testing.

The adapter for low temperature testing, shown in Figure 4, is mounted on the driven shaft of the Scott (*D*). A bar of flat steel, 1 inch by ¼-inch, is used as the supporting member (*S*) for a Dewar flask (*F*), containing alcohol, as well as serving as the lower grip for the test piece at (*L*). The upper end of the test-piece is mounted at (*U*) on the shaft (*R*), which connects to the recording dial. The thumb screws shown at (*U*) and (*L*) mount the piece securely and do not cause tearing at the low elongation employed in the test. The thermometer, stirring device and rule for following the elongation, have been omitted from the photograph for clarity.

A six-inch dumbbell test-piece, having a test-section ½-inch wide, is used. Holes for mounting the test-piece are punched 4½ inches apart in the tab ends.

Testing procedure.—Specimens are cut in the mill (grain) direction from regular ASTM test sheets, and thickness readings are made in the usual manner for tensile testing. A two-inch bench mark is placed near the middle of the test-piece, and the latter is then mounted for testing. The alcohol bath, at +25° C, is slid up into position on a clip provided for its support at (*C*). A rubber bumper (*B*) holds the flask in position. A stainless steel rule is placed in the bath to follow the elongation indicated by the bench mark. The test-piece, having never been stretched before, is given a preliminary stretch to 50 per cent elongation, after which it is allowed to condition for five minutes at +25° C. At the end of this period the tester is started, and the elongation is followed carefully. At 25 per cent elongation the tension is recorded by the sparking device on the chart of the Scott, and the tester immediately reversed.

After all test-pieces in the series have been tested in this manner at +25° C, the bath is cooled with dry ice to −25° C. Beginning with the first dumbbell tested, the procedure is repeated, taking care that the bath is stirred and held at −25° ± 0.5° C.

The M-25 value or percentage increase in stiffness with temperature drop from +25° to −25° C. is calculated:

$$\text{M-25} = \frac{M_2 - M_1}{M_1} \times 100,$$

where M_1 is the modulus in lbs. per sq. in., determined at +25°, and M_2 is the modulus determined at −25° C.

Low temperature stiffness data on the compounds described earlier are given in Table III, along with brittle points.

TABLE III

LOW TEMPERATURE STIFFNESS AND BRITTLE POINT RESULTS

Elastomer	Plasticizer	Modulus at 25% elongation (lbs. per sq. in.) +25° C	Modulus at 25% elongation (lbs. per sq. in.) −25° C	Increase	M-25 value	Brittle temp. (° C)
Natural rubber	5% coal-tar softener	145	175	30	21	−58
GR-S	5% coal-tar softener	115	195	80	70	−69
Perbunan	None	230	1760	1530	665	−50
Perbunan	30% Plasticizer A	90	170	80	89	−52
Perbunan	30% Plasticizer B	90	135	45	50	−62
Hycar OR-15	30% Plasticizer A	90	670	580	645	−39
Hycar OR-15	30% Plasticizer B	85	220	135	159	−49

DISCUSSION OF RESULTS

The comparative data in Table III illustrate the value of employing both brittle point and low-temperature stiffness measurements for more complete evaluation of the cold resistance of elastomers. It is interesting to note that natural rubber having a brittle point 11° higher than GR-S has an M-25 value of only 21, compared to 70 for GR-S.

Although Perbunan in the unplasticized state would never be considered for low-temperature service, it has been included here as an illustration of a material which has a low brittle point, yet would not have sufficient flexibility to be useful in a flexing application at low temperatures. The addition of 30 per cent of Plasticizer A, however, has a profound effect on low-temperature

stiffness, while depressing the brittle point only 2° C. In Perbunan, the effect of Plasticizer B is even more marked than that of Plasticizer A, since it improves brittle point as well as low-temperature stiffness. Again in Hycar OR, Plasticizer B is outstanding in improving an elastomer which stiffens more than Perbunan in the unplasticized state.

CONCLUSIONS

The illustrations indicate some of the possibilities in our method of evaluation. The urgency of the times requires that all workers come forward with any new test methods that may be of value in developing better compounds, without consuming valuable time investigating all of the possibilities and limitations of such methods.

Possibly other workers will wish to apply the methods described, in their studies on the effects of plasticizers, curing times and temperatures, reenforcing fillers, etc., in low-temperature compounding of the various new elastomers being pressed into service today.

ACKNOWLEDGMENT

We wish to thank R. Bowling Barnes and L. Boor for their suggestions and active interest in the development of these tests.

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THE EFFECT OF PETROLEUM SOLVENTS ON THE COLD RESISTANCE OF SYNTHETIC VULCANIZATES*

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Vulcanizates prepared from the oil-resistant synthetic rubbers are frequently called upon to withstand low temperatures in service. This is particularly true of applications in airplanes, although fairly low temperatures are also encountered in ground service or on shipboard. Oil and gasoline hose, for example, must remain flexible at low temperatures for ease in handling. Unfortunately all oil-resistant rubbers are affected adversely by low temperatures, much more so than *Hevea* rubber, and they require special compounding to improve their cold resistance[1]. The general practice has been to include certain ester-type softeners in the formulations for this purpose.

Gasolines and other light petroleum products are absorbed to some extent in all oil-resistant vulcanizates if the solvent is left in contact with the rubber for a length of time. Meanwhile the solvent gradually extracts the softeners from the rubber. The question is: Does the absorbed solvent have a beneficial effect on cold resistance, particularly in view of the fact that protective softeners may be extracted?

The lighter petroleum products have very low freezing points; for example, the freezing point of ordinary gasoline is below −100° F. Therefore their presence in the rubbers should be beneficial from the standpoint of cold resistance.

VULCANIZATES TESTED

To find the effect of absorbed solvent on the cold resistance of synthetic rubber vulcanizates, typical gasoline hose stocks were prepared from Neoprene-GN, Neoprene-ILS, Thiokol-FA, Hycar-OR-15, and Perbunan. The brittle points of these stocks were then determined before and after immersion at 82° F in isoöctane, 100-octane gasoline, and a blend of 100-octane gasoline with aromatics. The volume change and extraction by these solvents were also found.

Previous work indicated that thirty days was a sufficiently long time for these stocks to reach equilibrium with respect to volume change and extraction in these solvents. This being the case, it was reasonable to assume that the brittleness values for these stocks would also reach constancy in this time.

The recipes, optimum sheet cures, tensile properties, and Shore hardnesses of the stocks are given in Table I. None of these stocks was compounded especially for cold resistance. These stocks complied with the limitations on rubber content imposed by the War Production Board Supplementary Order

* Reprinted from the *India Rubber World*, Vol. 108, No. 6, pages 553–555, 558, September 1943.

TABLE I

RECIPES, CURES, AND SOME PHYSICAL PROPERTIES OF THE SYNTHETIC VULCANIZATES

Recipe	Neoprene-GN	Neoprene-ILS	Thiokol-FA	Hycar-OR-15	Perbunan
Neoprene-GN	100.0				
Neoprene-ILS		100.0			
Thiokol-FA			100.0		
Hycar-OR-15				100.0	
Perbunan					100.0
Semi-reënforcing black			75.0	80.0	80.0
Soft thermal black	125.0	100.0		40.0	40.0
Zinc oxide	5.0	10.0	10.0	5.0	5.0
Light calcined magnesia	4.0	10.0			
Stearic acid	0.5	0.5	0.5	1.0	1.0
Dibutyl phthalate				15.0	
Bardol					15.0
Circo light process oil	10.0				
Cumar P-25			5.0		
Advagum		30.0		25.0	25.0
Phenyl-alpha-naphthylamine	2.0	2.0		1.0	1.0
Di-*o*-tolylguanidine salt of di-catechol borate		1.0			
Benzothiazyl disulfide			0.3	1.75	1.75
Diphenylguanidine			0.1		
Micronized sulfur				1.75	1.75
Sheet cure					
Time (min.)	40	40	40	60	60
Temperature (° F)	287	307	298	274	274
Physical properties					
Tensile strength (lbs. per sq. in.)	1740	1530	1160	1720	1640
Ultimate elongation (percentage)	310	350	250	380	420
Shore hardness (¼-inch thickness)	69	67	73	65	64

M-15-b 1, Amendment 9. They also complied with the Bureau of Ships *ad interim* specification for smooth bore gasoline hose[2]. All of these stocks handled satisfactorily on the calender.

SOLVENT CHARACTERISTICS

A 100-octane gasoline (containing lead tetraethyl) and a blend of this gasoline with aromatics were employed as solvents in this test because these fuels are probably the most severe of any petroleum solvents in their action on hose tubes. The blend was made up of the following proportions by volume:

100-octane gasoline	60
Toluene	20
Xylene	15
Benzene	5

All of the aromatic components of this blend were the chemically pure grade. The aniline points and diesel indices of the 100-octane gasoline and the blend are given in Table II. These properties have been connected with the swelling power of solvents by Fraser[3].

Isoöctane was included in the study for an academic reason. It was desired to find what effect on brittle points would be obtained by a relatively pure aliphatic liquid of the type found in gasolines. This solvent was prepared by fractionating a technical grade of isoöctane and collecting the fraction boiling in the range 210–215° F[4]. The aniline point and diesel index of this

solvent are listed in Table II. The high aniline point of isoöctane is characteristic of an aliphatic compound.

APPARATUS FOR BRITTLENESS TEST

The brittleness test developed by Selker, Winspear and Kemp[5] with slight modification was employed as a measure of cold resistance. This test locates the temperature at which a rubber specimen cracks when bent rapidly around a small radius. This temperature, termed the brittle point, is a characteristic

TABLE II

PROPERTIES OF SOLVENTS

Solvent	Aniline point (° F)	Diesel index
Isoöctane	173.8	123.7
Gasoline	147.7	97.3
Gasoline-aromatic blend	61.7	31.1

property of every rubber, assuming that the rate and the radius of bending are held constant.

The apparatus consisted of an insulated steel tank, 18 by 2 by 8 inches. Seven inches from one end on the top was mounted a brass semicircle of 4.87-inch radius and 0.50-inch thickness, keyed to a shaft. Six notches, 0.25 inch deep and 0.075 inch wide, were spaced at two-inch intervals on the rim of the semicircle. Each notch was backed with a block extending 0.25 inch above the rim. A stiff ¼-inch round rod was fixed across the tank exactly 0.5 inch from the rim of the semicircle. The shaft on which the sample-holding fixture was mounted had a crank, which, on rotation, immersed the specimens in the tank. The shaft was supported on ball-bearings.

A suitable liquid, cooled by adding lumps of dry ice, was used as the immersion medium. The liquid was circulated by an air-driven stirring motor. The temperature of the liquid, determined with a thermocouple, was raised rapidly when desired by adding warm liquid or inserting a 500-watt immersion heater in the bath.

Photographs of the apparatus are shown in Figures 1 and 2. Figure 1 shows the insulated tank, the brass semicircle with six specimens in position for breaking, the crank, and the air-operated stirring motor. Figure 2 shows a closeup of the specimen striking the round rod. In Figure 2 may also be seen the support for a thermometer, although, as mentioned above, the authors preferred to use a thermocouple for measuring the temperature of the solvent.

A close-fitting sheet metal hood was placed over most of the tank after insertion of the specimen to prevent splashing the alcohol out of the tank when the crank was turned rapidly. This hood is not shown in the photographs.

TREATMENT OF SPECIMENS

Specimens, one inch by two inches, were died from sheets 0.08 inch thick, which had been lightly buffed on both sides. The original brittle point of each stock was found by using some of these specimens. Then the volumes of fifteen of these specimens from each stock were determined with a Jolly balance, and the specimens were immersed individually in 100 milliliters of each solvent in separate containers. Thus two hundred and twenty-five containers were required for this test. The containers were tightly closed and let stand for thirty days at 82° F, plus or minus 5° F.

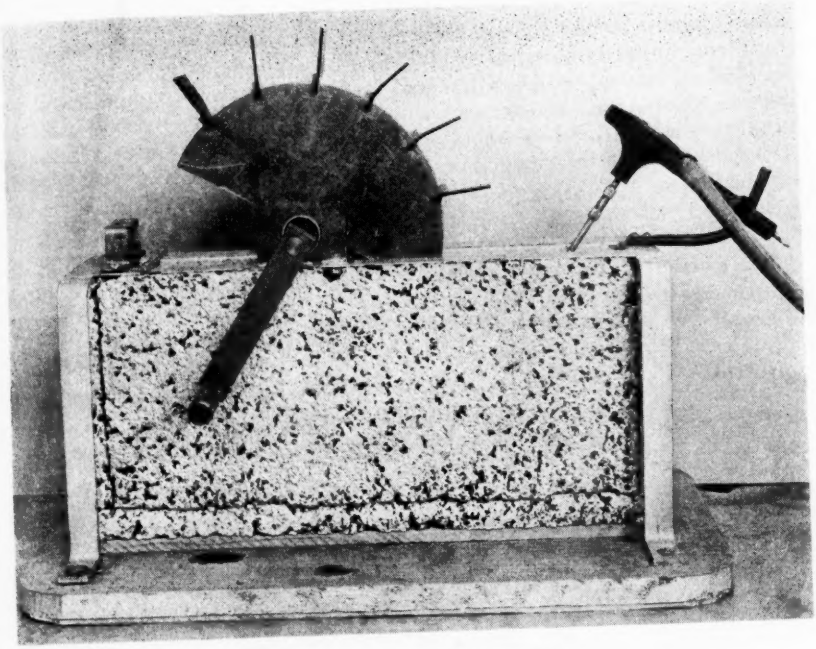

FIG. 1.—The brittle point apparatus.

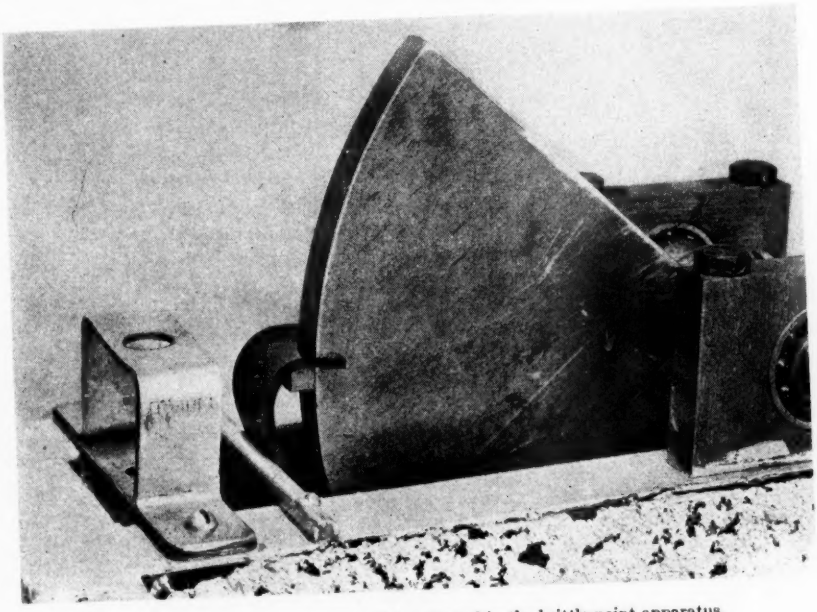

FIG. 2.—Closeup of specimen striking the rod in the brittle point apparatus.

At the end of the thirty-day period, the volumes of the specimens were measured again to find the volume changes, and then the brittle points were determined immediately in a cold bath of the same solvent, in which the respective specimens had been immersed. During the several minutes between these operations, the specimens were immersed again in the respective solvents so that no evaporation loss would occur from the specimens themselves. The extracted materials in the solvents were found by a procedure which will be described later.

DETERMINATION OF BRITTLE POINTS

The brittle points were ascertained by the following procedure. One end of a specimen was inserted into a notch on the rim of the semicircle by grasping the corners with pliers and stretching the rubber so as to decrease its thickness and allow it to slip freely into the notch. When the tension was relaxed, the rubber formed a snug fit in the notch and overlapped ¼ inch on each side of the semicircle. It was found advisable to insert and test only one specimen at a time on the rim of the semicircle to obtain maximum velocity of impact.

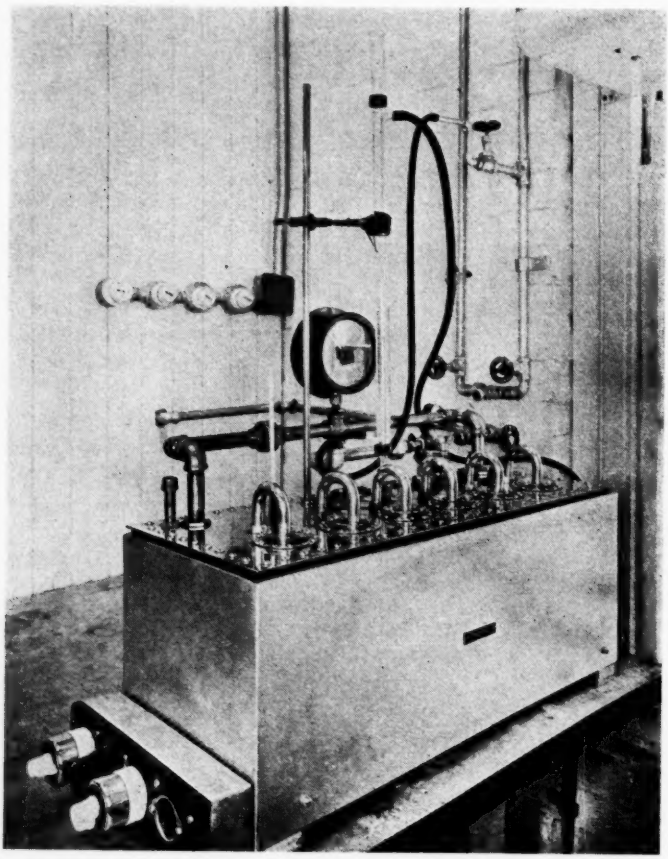

FIG. 3.—Apparatus for A. S. T. M. evaporation of gasoline for determination of gum content.

The tank was filled to within three inches of the top with liquid, which was cooled to the desired temperature by chunks of dry ice. The cooled liquid was circulated by means of the stirring device. When the liquid had arrived at the desired temperature, the semicircle was turned so that the specimen was immersed in the cold liquid. Exactly two minutes after the specimen was immersed, the crank was turned rapidly in a clockwise direction so that the specimen struck the horizontal bar just as it rose out of the liquid. The temperature at which the specimen was cracked by this treatment was considered to be the brittle point of the rubber. It was found that the brittle points of different specimens of the same stock generally agreed within 1.0° F.

DETERMINATION OF EXTRACTABLE MATERIALS

The extracted material in the solvents was found by evaporating the respective solvents to dryness in tared 100-milliliter beakers, according to the A. S. T. M. standard method of test for gum content of gasoline[6]. In this method the gasoline contained in a beaker is evaporated by placing the beaker into a well over a bath maintained at 320 to 330° F. During the evaporation a blast of air at the same temperature as the bath blows over the gasoline. After the gasoline has evaporated, the beaker is heated for an additional 15 minutes; then it is cooled and weighed. The apparatus used for this evaporation is shown in Figure 3. The advantage of employing this evaporation procedure over the procedure generally described in specifications will be the subject of another paper.

INITIAL BRITTLE POINTS

There was some question as to the correct liquid to use in the cooling bath when determining the initial brittle points. Methyl alcohol and the three petroleum solvents were tried. The results are given in Table III. It will be

TABLE III

EFFECT OF SOLVENT ON ORIGINAL BRITTLE POINT

Vulcanizate	Brittle point (° F)			
	Methyl alcohol	Isoöctane	Gasoline	Gasoline-aromatic blend
Neoprene-GN	−32	−35	−35	−39
Neoprene-ILS	18	20	17	15
Thiokol-Fa	−27	−24	−24	−26
Hycar-OR-15	0	8	4	3
Perbunan	−17	−21	−19	−18

noted that the brittle points found depended on the liquid used. For example, the Hycar-OR-15 stock showed a brittle point 8° F higher in isoöctane than in methyl alcohol. This behavior indicated that more permeation of the cooling liquid into the rubber occurred during the two-minute cooling period in the case of the specimens of each stock which showed the lower brittle points. In support of this statement, it was found by measurement that the Hycar-OR-15 stock was swollen 4.6 per cent by methyl alcohol in two minutes at room temperature, but only 0.7 per cent by isoöctane.

It was decided to consider the highest brittle point found for each stock as the correct value. Thus the values found in methyl alcohol were regarded as correct for the Neoprene-GN and Perbunan stocks, and the values found in

isoöctane were regarded as correct for the Neoprene-ILS, Thiokol-FA, and Hycar-OR-15 stocks.

RESULTS OF TESTS

The brittle points, before and after immersion in the various solvents, are graphed in Figure 4. The volume change and extraction data are given in

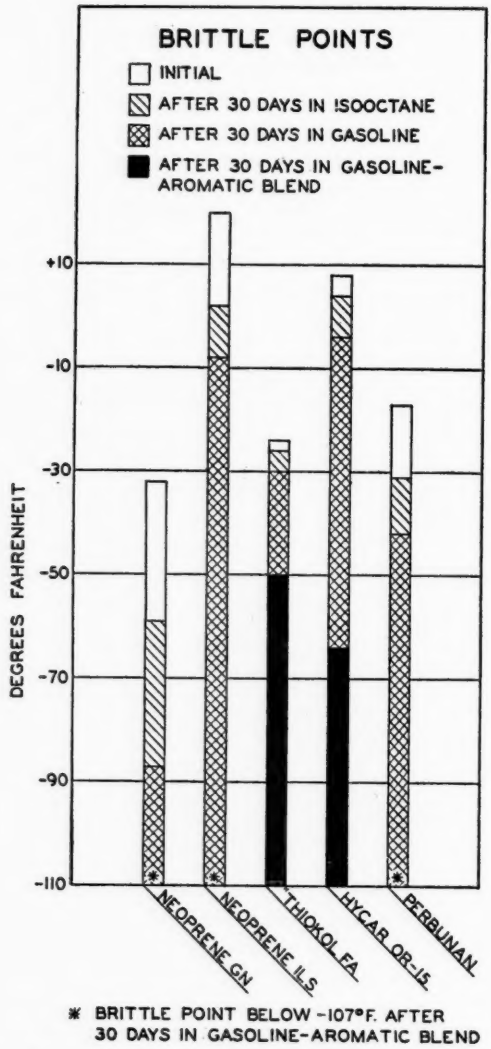

FIG. 4.—Brittle points before and after immersion in the various solvents.

Table IV. The bar graph and the volume change data indicate clearly that immersion in petroleum solvents lowers the brittle point and that the greater the swelling, the greater the brittle point lowering. This relation was par-

ticularly evident in the cases of the Neoprene-GN, Neoprene-ILS, and Perbunan specimens after immersion in the gasoline-aromatic blend. These specimens were considerably swollen, and had lower brittle points than could be reached by dry ice in that solvent.

TABLE IV

VOLUME CHANGE AND EXTRACTION DATA

Vulcanizate	Isoöctane		Gasoline		Gasoline-aromatic blend	
	Volume change (%)	Extraction (%)	Volume change (%)	Extraction (%)	Volume change (%)	Extraction (%)
Neoprene-GN	6.7	1.5	15.4	2.3	75.7	2.9
Neoprene-ILS	−0.4	0.4	2.7	1.0	23.2	3.4
Thiokol-FA	−1.2	0.6	0.1	0.9	7.8	2.4
Hycar-OR-15	−2.4	0.6	−1.3	0.7	7.1	4.0
Perbunan	−2.5	1.6	0.1	2.6	30.4	4.4

The aniline point or diesel index of the solvents can be correlated with the behavior of the vulcanizates in the solvents. The lower the aniline point or diesel index of the solvent, *i.e.*, the greater the aromatic content, the greater the volume changes in a positive direction of the vulcanizates and the lower their brittle points. Isoöctane, a 100 per cent aliphatic compound, possesses a high aniline point and a high diesel index; accordingly, it had the least effect on the brittle points of the vulcanizates.

The volume changes of all except the Neoprene-GN stock were negative in isoöctane. This behavior was due to the extraction of softeners, although the weight of softeners removed according to the A. S. T. M. evaporation method was generally less than was indicated by the shrinkage in volume, assuming a reasonable specific gravity for these materials. Apparently some of the softeners were lost by evaporation or sublimation during evaporation of the solvent. At any rate the amount of material extracted from the rubbers increased in every case as the aniline point of the solvent decreased.

CONCLUSION

It is concluded that immersion in light petroleum solvents improves the cold resistance of synthetic vulcanizates, and that the greater is the aromatic content, *i.e.*, the lower the aniline point, of the solvent, the greater will be this improvement.

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SIMPLE VULCANIZATES OF BUNA-S AND SULFUR

PHYSICAL AND CHEMICAL PROPERTIES *

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The earliest vulcanizates of rubber consisted of only two ingredients, rubber and sulfur. Actually, at least one other ingredient, fat acid, was probably present in the so-called acetone extract of the rubber. However, it was not long before the use of other compounding ingredients, especially inorganic accelerators, was developed.

After the introduction of organic accelerators[1], most rubber goods were compounded with them, together with various activators. Simple products containing only rubber and sulfur were practically forgotten. Those in the ebonite range, however, were found to possess interesting properties and were studied in more detail[2].

The only studies of the simple rubber-sulfur system over the entire range from soft to hard rubber have been those concerned chiefly with the mechanism of vulcanization. Houwink[3] presents graphically the variation of stress-strain properties with sulfur content. Blake[4] and Jessup and Cummings[5] present data for such a series, although their samples were vulcanized to the absence of significant sulfur in the free state.

Most of the reported work on the compounding of Buna-S has, under the pressure of wartime necessity, been concerned with the substitution of this polymer in accelerated formulas which can be processed and handled in conventional rubber equipment and which involve little change in operating technique[6].

A few investigators have published isolated bits of information concerning ebonites prepared from the various butadiene polymers[7]. Klebsattel[8] mentions some characteristics of Perbunan vulcanizates containing intermediate sulfur contents (10–15 per cent on the polymer) and indicates them to be superior to the corresponding rubber products. Most of these data were obtained on accelerated stocks, and consequently provide little direct information on the simpler combination between Buna-S and sulfur in the absence of other compounding ingredients.

This investigation was undertaken to obtain information on the simpler system and to attempt to fill in a few of the many gaps in the existing knowledge of Buna-S vulcanization. It seemed possible that such data might also provide additional evidence toward an elucidation of the mechanism of vulcanization in general.

* Reprinted from *Industrial and Engineering Chemistry*, Vol. 35, No. 9, pages 976–979, September 1943. This paper was presented before the Division of Rubber Chemistry at the 105th Meeting of the American Chemical Society at Detroit, Michigan, April 15–16, 1943.

The problem is divided into two parts: (1) a study of the physical and chemical properties of vulcanizates containing various percentages of combined sulfur and (2) measurement of the heats of combustion of these vulcanizates to provide data on the thermal relations involved in the vulcanization. Thermal measurements will be the subject of a second paper. Some of the data in this section are not so complete as might have been desired because the same set of samples had to be used for both series of measurements.

EXPERIMENTAL PROCEDURE

The major portion of the experimental work was performed at the University of Akron; owing to the departure of both authors from the university, some of the information which might have aided in creating a more complete picture of this system was not obtained. It is believed, however, that the data are of sufficient interest to warrant their presentation, if only for the reason that data on such relatively simple systems are lacking in the technical literature.

The Buna-S used was a typical batch of American factory production, supplied by The Firestone Tire & Rubber Company in February, 1942. It was compounded, as received, with the desired amount of sulfur, and the uncured stocks were stored between sheets of heavy parchment paper until used. Stocks were compounded to contain 2.5, 5.0, 10.0, 15.0, 25.0, and 35.0 per cent sulfur. These correspond to "coefficients of vulcanization"[9] of 2.57, 5.26, 11.11, 17.65, 33.33, and 53.85, respectively.

Press-cures were carried out by the recommended A. S. T. M. procedures[10] for 2, 4, 6.5, and 10 hours at 315° F. In the samples containing 15 per cent or more of sulfur, vigorous evolution of hydrogen sulfide was observed during the cures; this was most pronounced in the 35 per cent sample.

Stress-strain properties were measured by the A. S. T. M. procedure[11]. Hardness was determined by the method of Cooper[12], with a Shore durometer calibrated by the method of Larrick[13]. Densities were measured by an adaptation of the hydrostatic method of Wood, Bekkedahl and Roth[14], using a Saran filament for suspension of the sample and sinker.

"Free" sulfur was determined in the acetone extract by the A. S. T. M. bromine oxidation method[15]. This value actually represents not only free sulfur, but also that in any form of combination which is acetone-soluble. Combined sulfur was determined on the extracted samples by the method of Cheyney[16]; this value is likewise a function of solubility relations. Nevertheless, these extracted samples were employed for some of the thermal measurements, and it was desirable to obtain the analytical data for the same samples.

The extractions were carried out for 72 hours to eliminate any differences between the soft and hard samples because of different degrees of extraction. The extracts from all samples increased on continued extraction, but tended to approach constant values after about 60 hours. Several samples were also extracted exhaustively with ethanol, and the extract values in all cases were somewhat lower than those obtained with acetone. It is believed that the acetone may exert a solvent action on certain of the hydrocarbon fractions, similar to the effect noted with methylethyl ketone on natural rubber[17]. It is also believed that ethanol is, in general, a somewhat safer solvent to employ for extraction of this type of polymer, as it seems to have no solvent action on the polymer itself.

The ash determinations were made by the A. S. T. M. procedure, without variation.

ANALYTICAL DATA

Table I and Figure 1 give the analytical data, which are the averages of several determinations in each case. The actual percentages of combined sulfur in the extracted samples show good agreement with that compounded, except in the 35 per cent sample. Here a considerable amount of substitution

TABLE I

ANALYTICAL DATA ON 6.5-HOUR CURES

Sulfur (percentage as compounded)	0	2.5	5	10	15	25	35
Acetone extract (calculated on original polymer)	11.91	10.31	9.30	7.45	6.78	6.30	5.12
Ash (calculated on original polymer)	0.64	0.65	0.65	0.50	0.49	0.38	0.37
Free sulfur	0.22	0.17	0.20	0.19	0.14	0.19	0.58
Combined sulfur	0.74	2.70	5.37	9.88	14.72	23.65	31.04
Density (measured)	0.930	0.943	0.971	0.971	1.003	1.090	1.170
Density (calculated)	...	0.944	0.966	0.983	1.012	1.078	1.152

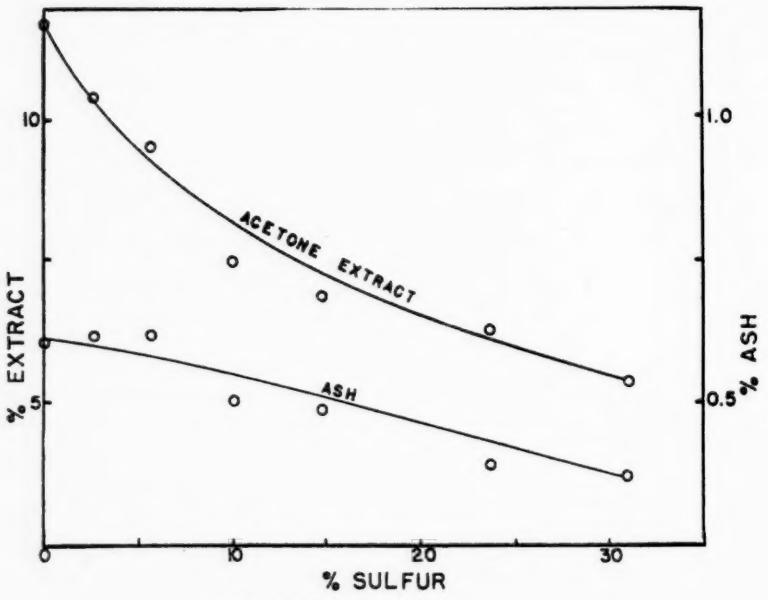

FIG. 1.—Analytical data on 6.5-hour cures.

must have taken place, with the liberation of a large amount of hydrogen sulfide. However, all of the samples containing more than 5 per cent sulfur give analytical figures less than the calculated values, especially when one adds to the sulfur as compounded the value of the blank in the original sample.

The presence of sulfur in the original sample is interesting, especially since a portion of it is in the acetone-insoluble or "combined" state. This presumably originated from the use of sulfur-containing substances in the polymerization process. This is not new practice[18]. Olefins have been shown to react with various sulfur compounds and even with sulfur itself[19], so it is not

surprising to find some of the sulfur in combined form. The determination of the actual form in which it is present would be the subject of a separate problem and would require the use of considerably larger quantities of material. Probably it is present in more than one form of combination.

The progressive diminution of the acetone extract (Figure 1), even when calculated in terms of the original polymer as compounded, is an indication that some reaction of the soluble material is taking place. This might involve

TABLE II

PHYSICAL PROPERTIES OF CURED STOCKS

Sulfur content (percentage)	Time of cure (hours)	Tensile strength (lbs. per sq. in.)	Elongation (percentage)	Tensile product $\times 10^{-4}$	Shore hardness
2.5	1	140	400	5.60	34
	2	148	385	5.70	38
	4	200	260	5.22	45
	6.5	175	210	4.80	50
	10	240	200	3.68	52
5	1	120	325	3.88	36
	2	160	325	5.20	45
	4	190	265	5.04	53
	6.5	200	250	5.00	59
	10	212	204	4.32	63
10	1	155	200	3.10	43
	2	250	130	3.25	55
	4	360	125	4.51	67
	6.5	480	120	5.75	70
	10	465	110	5.12	72
15	1	200	175	3.50	49
	2	375	150	5.62	65
	4	1680	125	21.0	98
	6.5	1860	60	11.5	100
	10	2960	20	5.92	100
25	1	200	175	3.50	55
	2	1680	75	12.00	100
	6.5	6077	9	5.35	100
35	6.5	6182	8	5.25	100

polymer fractions originally soluble in acetone which could be combining with sulfur or which might merely be undergoing further thermal polymerization. Either reaction could give rise to a less soluble product. The progressive character of the effect with increasing proportions of sulfur tends to favor the hypothesis that the sulfur is involved in the reaction. The extract value seems to be approaching a constant figure of 5–6 per cent which is presumed to represent nonpolymer material originally present.

A similar effect, although less pronounced, is observed with the ash contents of the various samples (Figure 1). Here again the percentage calculated in terms of original polymer as compounded shows a progressive diminution with increasing sulfur content of the sample. This is more difficult to explain. Qualitative examination of the ash from the uncompounded sample indicated that it consisted largely of oxides of iron and aluminum. No ready explanation suggests itself to explain the apparent disappearance of this material with

increasing sulfur content. The magnitude of the analytical figures is not great and hence the differences are not pronounced. It is possible that they may be due to experimental error, although the error should be somewhat less than the recorded differences. The ash values reported are the average of duplicate determinations, which show reasonably good agreement. However, the reported values do not fall so readily on a smooth curve as do those of the extracts, nor is the accuracy so great. No real significance can therefore be justifiably attached to this variation. One possibility is a variable conversion to sulfates during the ashing procedure, even though the latter was supposedly carried out under constant conditions. Insufficient sample was available to investigate this question to any greater extent.

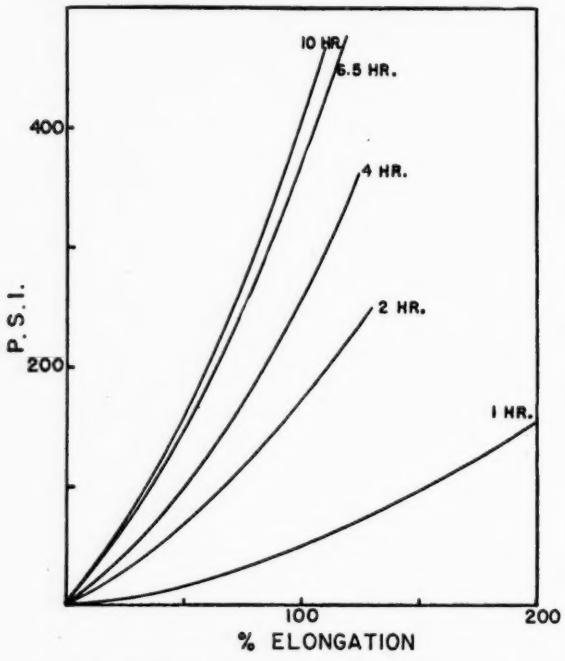

FIG. 2.—Stress-strain curves for 10 per cent sulfur sample.

The densities of the vulcanized samples showed reasonable agreement with those of the unvulcanized, which in turn agreed with the calculated values. Two generalizations are evident: (1) there is no appreciable change in density on vulcanization; (2) no discontinuity is evident in the density curve, such as might be produced by major changes in structure of the polymer during some stage of the vulcanization.

PHYSICAL PROPERTIES

The data are listed in Table II. The stress-strain curves are plotted in Figure 2 for a typical member of the series, the 10 per cent sulfur sample. Those for the other members of the series are similar. The most striking feature is the low value of both the ultimate tensile and elongation. This

agrees with data reported by other investigators for pure-gum accelerated stocks[20].

The variation of stress-strain properties with sulfur content (Figure 3) shows an interesting relation. In this connection it is worth recalling the shape of the similar curves for natural rubber[21]. The only region of resemblance is in the true ebonite region of about 25 per cent or more combined sulfur, where both rubber and Buna-S give products of high tensile strength and low elongation. In the soft natural rubber region, a maximum tensile strength is reached at slightly less than 6 per cent sulfur, after which both

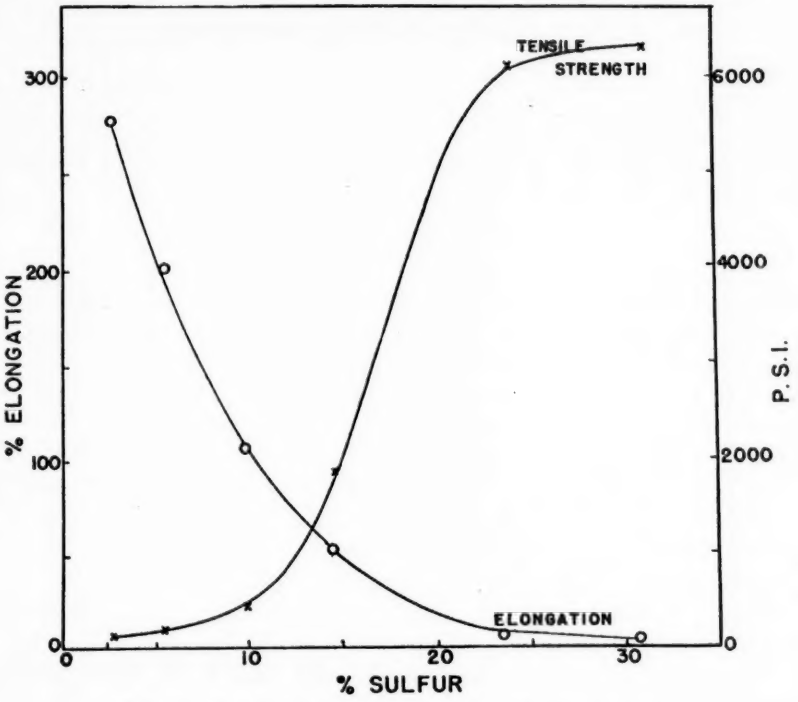

FIG. 3.—Variation of stress-strain properties with sulfur content.

tensile strength and elongation fall off rapidly. The intermediate stage, called semiebonite by Gibbons, is characterized as leathery in that the products possess both low tensile strength and elongation.

In the Buna-S series, however, the only resemblance to a leathery character is to be found in the early members of the series, which possess low tensile strength, coupled with moderate elongation. The tensile strength increases concurrently with a progressive decrease in elongation as the sulfur content increases. The trend of elongation is somewhat similar to that of the rubber series, although at no time do elongations approach those of the rubber samples. It should be noted that the stress-strain data of Houwink[3] are calculated in terms of final rather than original cross-section. The general character of the curve of rubber is not altered significantly by this difference.

The trend of the property known as tensile product bears a direct relation to the ultimate tensile strength, expressed in terms of breaking cross-section[22]. Since a limited series of cures was available for the hard samples, it cannot be assumed that the maximum tensile product was obtained in all cases. The maximum tensile product for the 15 per cent sulfur sample was for a cure still definitely in the soft rubber stage. As the sample hardens, the elongation decreases more rapidly than the tensile strength increases, with a consequent drop in tensile product.

In general, the hardness values show the same trend as those of tensile strength. Modulus of elasticity figures are of little value over a wide range of properties such as these samples exhibit and since, like natural rubber, Buna-S apparently does not follow Hooke's law, no further interest in this property was manifested.

This study leaves questions unanswered on other physical properties, such as cold flow, brittle point, aging properties, etc. Additional analytical data on some of the samples would be desirable. It should be emphasized that these data were all obtained with a single batch of polymer and that considerable variation could be expected in any work with other batches.

ACKNOWLEDGMENT

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STUDIES IN COMPOUNDING GUAYULE RUBBER

I *

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With the loss of the Malayan Peninsula and the Dutch East Indies, the United States and her Allies have been deprived of about 97 per cent of their crude rubber supply. This fact explains in part the revived interest in guayule rubber. Of all the known rubber-bearing plants besides *Hevea*, it is the most promising from the point of view of yield and because it can be cultivated within our own borders.

Although considerable literature pertaining to plant biological aspects of guayule and its cultivation has accumulated, very little has been published[1] on the processing properties of guayule rubber and the properties of articles made from it. This is especially deplorable because the few available publications are contradictory and not directly comparable, because of different types or grades of guayule rubber having been used.

DERESINIFIED DOMESTIC GUAYULE PURE-GUM COMPOUND USED

To avoid unnecessary complicating factors and to facilitate comparison with the processing and mechanical properties of *Hevea* rubber (standard prime ribbed smoked sheet) it was decided to use, at least for the first part of this investigation, a simple pure-gum mixture. The following formula, unless otherwise indicated, was used throughout this investigation. The rubber was commercially available deresinified guayule obtained from the Salinas, California, plant of the Continental Rubber Co. of New York. The resinous substances still present in this product amounted to 6 per cent.

Deresinified guayule	100
Sulfur	3
Mercaptobenzothiazole	1
Stearic acid	1
Zinc oxide	5

No antioxidant was added, since deresinified guayule itself contains sufficient.

This formula was decided upon after stepcures at 290° F had shown that the compound containing three parts of sulfur exhibited the best overall curing characteristics (see Table 1).

Table 1

Minutes' cure	Total sulfur (percentage)	Free sulfur (percentage)	Combined sulfur (percentage)	Acetone extract (percentage)	Acetone extract (corrected) (percentage)	Elongation at break (percentage)	Tensile strength (lbs. per sq. in.)
5	3.24	1.82	1.42	8.13	6.3	835	1700
15	3.24	0.63	2.61	6.83	6.2	790	1795
30	3.24	0.28	2.96	6.41	6.1	790	1505
60	3.24	0.25	2.99	5.85	5.6	780	1095

* Reprinted from the *India Rubber World*, Vol. 106, No. 5, pages 447–449, August 1942. Part I is based largely on data of H. M. Zimmerman (M.S. Thesis, Mass. Inst. Tech., 1942) and of R. M. Haden of the Continental-Mexican Rubber Co. in experimentation at the Massachusetts Institute of Technology, May 1942.

These figures show some interesting facts. The compound is comparatively fast curing, and exhibits a pronounced drop in tensile properties after a 15-minute cure. Sulfur combination is very rapid at the start. Elongation remains practically constant, even after the maximum tensile strength has been reached.

EFFECT OF RUBBER BREAKDOWN ON TENSILE STRENGTH

During milling (using a mill at 100° F), it was noticed that guayule rubber broke down much faster than smoked sheet, and it is possible that this rapid breakdown may be largely responsible for the low tensile properties after vulcanization.

Since it is well known that the actual breakdown of rubber during milling decreases with increasing mill temperature, it was decided to run a second series of tests with the same compound, but breaking the guayule down on a

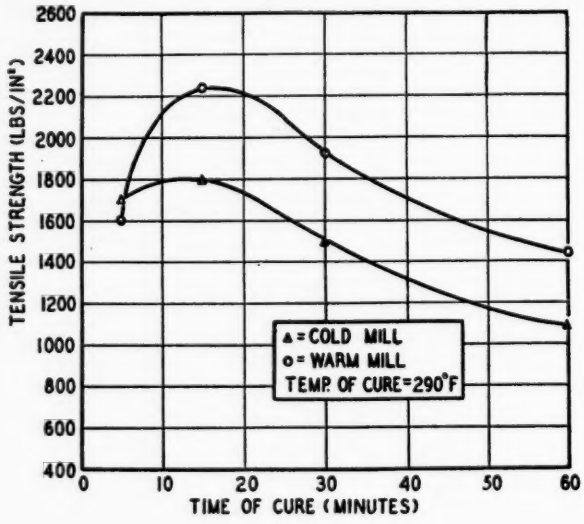

FIG. 1.

mill heated to 140° F. The time of compounding, size of the batch and mill gap were kept constant throughout. The results are shown in Figure 1 in comparison with those discussed above.

It is evident that the maximum tensile strengths were increased noticeably. There is no change in the rate of cure, and prolonged vulcanization results in an appreciable drop in tensile properties. The rate of sulfur combination remains unchanged, whereas the acetone extract is definitely lower in this series.

EFFECT OF CURING TEMPERATURE

Inasmuch as a breakdown of rubber can be achieved by heat as well as by mechanical treatment (milling), it was decided to reduce the curing temperatures in the next series of tests. The results are given in Figure 2.

It is evident that the curing temperature has a very decided influence on the vulcanization characteristics and physical properties of the mixture. As

the lowest curing temperature resulted in an extremely slow vulcanization, it was decided to use a temperature of 270° F and a mill temperature of 140° F in further work.

EFFECT OF INCREASED STEARIC ACID

Improved tensile strengths can be obtained by increasing the proportion of stearic acid to 1.5 parts per 100 parts of guayule[2], as is proved by a series of experiments in which the amount of stearic acid was gradually increased to as much as five parts per 100 parts of guayule.

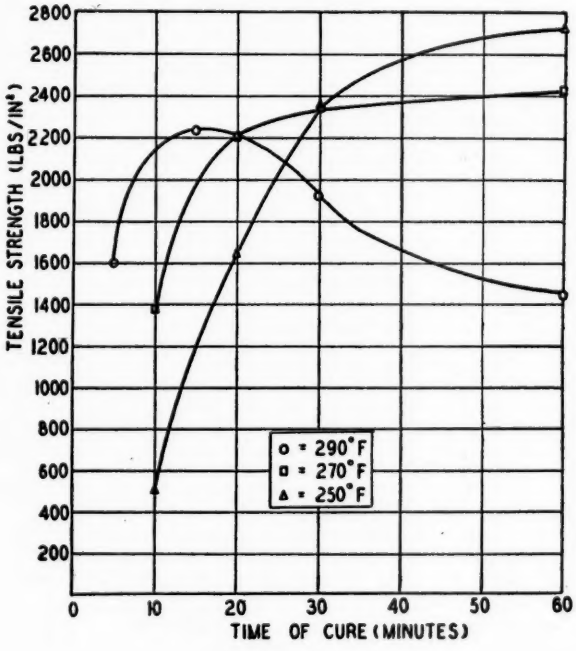

FIG. 2.

Figure 3 shows the results obtained with the standard mixture by varying the stearic acid from one part to four parts. The compound containing five parts of stearic acid shows a pronounced drop in tensile strength, and therefore has been omitted. Two points of importance are evident. The rate of cure is noticeably increased when the stearic acid is raised to 1.5 parts. Further increase to four parts does not appreciably change the rate of cure, but the tensile strength continues to increase; on the other hand, the elongations decrease with increasing stearic acid.

FURTHER EXPERIMENTS TO DETERMINE BEST CURING CONDITIONS

An interesting phenomenon is revealed when the proportion of stearic acid and the percentage acetone extract (corrected for the presence of free sulfur) of the cured compounds are correlated (Figure 4). The figures for the acetone extract pass through a definite minimum with two parts of stearic acid. This

result, in conjunction with the previously discussed improvements in tensile properties with increasing stearic acid, seems to indicate that a certain amount of acid is used up before it affects the vulcanization of guayule rubber.

Inasmuch as compounds containing small proportions of stearic acid have poor tensile strengths, and as it has also been found that the addition of small percentages of guayule resin to standard smoked sheet mixtures drastically

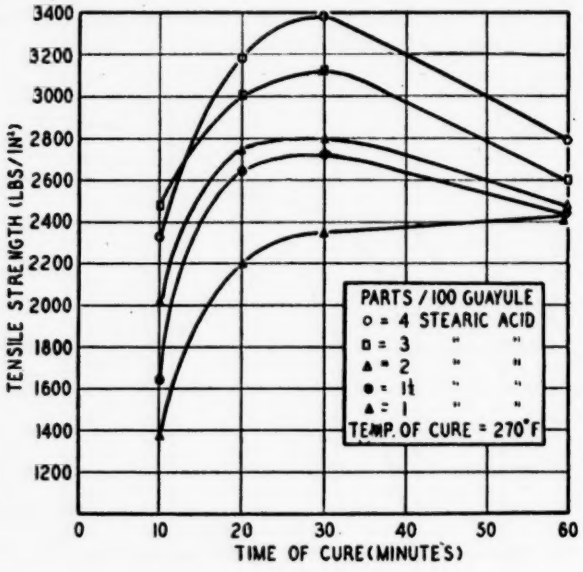

FIG. 3.

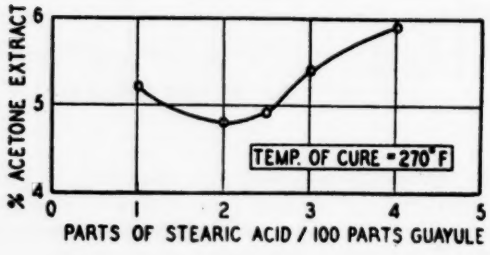

FIG. 4.

reduces their tensile properties[3], it is probable that stearic acid reacts with some component of the resin and forms an acetone-insoluble product. The results seem to indicate also that this resin component inhibits vulcanization. Moreover, preliminary experiments indicate the possibility of a resin-sulfur combination rather than a rubber-sulfur combination in the early stages of cure. This, and the added fact that guayule rubber seems to be decidedly more sensitive to thermal breakdown, suggest the importance of high speed-low temperature cures. To test this assumption, the following compounds were prepared:

A		B	
Guayule rubber	100	Guayule rubber	100
Sulfur	2.5	Sulfur	3
Zinc oxide	5	Zinc oxide	5
Stearic acid	4	Stearic acid	4
Mercaptobenzothiazole	1.5	Mercaptobenzothiazole	1
Diphenylguanidine	0.6	Diphenylguanidine	0.2

TABLE 2

	Cure (min.)	Tensile strength (lbs. per sq. in.)	Elongation at break (percentage)
Compound A (curing temp. 250° F)	20	4000	690
	30	3680	670
	40	3480	640
Compound A (curing temp. 230° F)	25	3970	720
	32	3980	690
Compound B (curing temp. 270° F)	5	3200	820
	10	3600	770
	15	3440	720

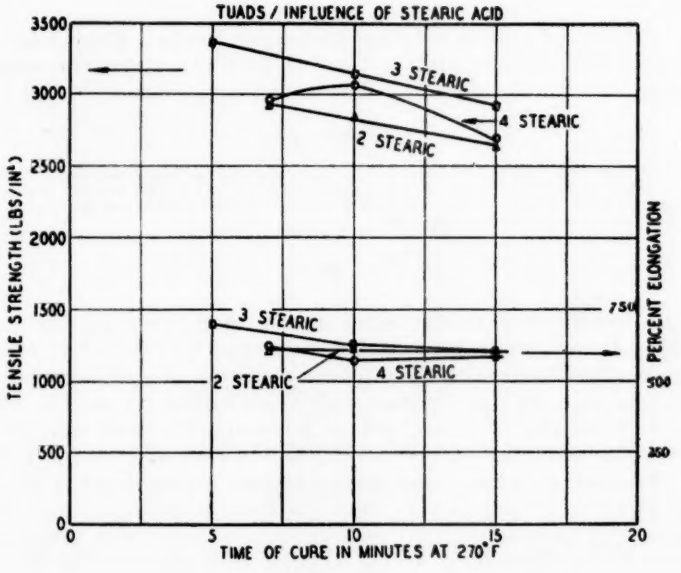

FIG. 5.

It is evident that the tensile properties have again increased and that low curing temperatures are beneficial. The data for Compound A indicate that the combined accelerators have resulted also in an increased rate of cure, but further work is necessary to ascertain the actual maximum. Likewise, the results for Compound B call for a repetition at lower curing temperatures.

Three more compounds were prepared to study the effect of stearic acid in a mixture containing tetramethylthiuram disulfide as accelerator.

	Compound C	Compound D	Compound E
Guayule (deresinified)	100	100	100
Sulfur	3	3	3
Zinc oxide	5	5	5
Stearic acid	2	3	4
Tetramethylthiuram disulfide	0.8	0.8	0.8

The results are given in Figure 5. They seem to indicate that the percentage of stearic acid necessary to give maximum tensile properties in mixtures accelerated with tetramethylthiuram disulfide is only three parts per 100 parts of guayule rubber and that a curing temperature of 270° F is too high, or that the percentage of accelerator should be reduced.

CONCLUSIONS

The authors consider the data presented by no means complete. However, they believe it their duty to publish the data available to show that guayule rubber cannot be processed, compounded, or vulcanized by standard *Hevea* rubber methods if maximum physical properties are desired and that, with appropriate mixtures, commercially deresinified guayule gives cured products equal in physical properties to those prepared from *Hevea* rubber.

ACKNOWLEDGMENT

The authors are greatly indebted to the Continental Rubber Co. of New York and to the Continental-Mexican Rubber Co. for the data obtained by Mr. Haden, and for the supply of deresinified guayule used in this work.

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[3] Smolka, M.S. Thesis, Mass. Inst. Tech., **1942**.

II *

Certain peculiarities in the compounding of guayule rubber have been described in Part I, and it has been demonstrated that the effect of increased proportions of stearic acid on the physical properties of a rubber mixture is far more pronounced with guayule than with *Hevea* rubber. Guayule, when compounded with one part of stearic acid per 100 parts of commercially deresinified guayule rubber, show an extreme retardation of cure and poor physical properties. However, guayule compounds containing higher proportions of stearic acid exhibit curing properties very similar to those of *Hevea* rubber. Inasmuch as commercially deresinified guayule still contains 6 per cent acetone-extractable resin, it was difficult to decide whether these peculiarities are inherent characteristics of guayule rubber hydrocarbon—which has a considerably lower molecular weight than that of *Hevea* rubber—or whether they are connected with the resin still present in the rubber. The difference in behavior during cure might be explained on the assumption that a chemical reaction occurs between the resin and the stearic acid, whereby the rubber is deprived of the well-known effect that stearic acid exerts during vulcanization. In this connection, it should be of interest to ascertain if this reaction is typical of stearic acid alone, or if it is a group reaction of fatty acids.

* Reprinted from the *India Rubber World*, Vol. 106, No. 12, pages 568–570, March 1943. Part II is based largely on data of E. H. Stewart, Jr. (B.S. Thesis, Mass. Inst. Tech., 1943).

To answer this question, it was decided to extract resin from nonderesinified guayule rubber and incorporate it into *Hevea* rubber (prime ribbed smoked sheet). *Hevea* rubber so resinified was then further compounded and tested in the customary way.

EXPERIMENTAL PROCEDURE

Resiniferous crude guayule, obtained from the Continental Rubber Co. of New York, was extracted with acetone, the acetone extract was dried in a vacuum, and the residue, a dark green, sticky mass of very strong aromatic odor[1], was stored in dark containers to avoid oxidation by light.

Prime ribbed smoked sheet was compounded according to the following formulas, which served as controls for all other mixtures[2].

	Parts
Smoked sheet	100
Zinx oxide	5
Mercaptobenzothiazole	1
Sulfur	3
Stearic acid	1, 4 and 6

Mill temperature	115° F
Curing temperature	270° F

Increased proportions of stearic acid resulted in increased tensile strength, as can be readily seen. The rate of cure was not affected (see Table 1).

TABLE 1

	Tensile strength at break (lbs. per sq. in.)			Elongation (percentage)		
	20 min.	40 min.	40 min.	20 min.	40 min.	60 min.
Control compound with						
1 part stearic acid	2350	3000	2800	800	820	800
4 parts stearic acid	2300	3500	2900	750	740	700
6 parts stearic acid	3200	3900	3600	760	770	710

STEARIC ACID IN "RESINIFIED" SMOKED SHEET

Similar mixtures, containing one part, two, four, and six parts of stearic acid, respectively, were prepared, and five parts of guayule resin was added to each mixture on the mill. The milling and curing temperatures were the same as for the control mixtures. The physical properties of these mixtures are shown in Figure 1.

It is evident that the tensile strength of the "resinified" mixture containing one part of stearic acid is only about 55 per cent of that of the corresponding control, as given in Table 1, and that the rate of cure of the former is considerably less. The "resinified" mixture containing two parts of stearic acid corresponds in its tensile strength to the control mixture with one part of stearic acid. Its rate of cure, however, also dropped appreciably. Contrary to the results obtained with the controls, no further rise in tensile strength occurs with increasing proportions of stearic acid. The rate of cure of the "resinified" mixtures rises steadily with increasing proportions of stearic acid. A "resinified" mixture containing six parts of stearic acid cures at the same rate as the control mixture.

Contrary to this, previous experiments on the compounding of commercially deresinified guayule showed that any increase in stearic acid above four parts

does not result in a further increase of physical properties. But the rate of cure did not change so markedly either in mixtures with two or four parts of stearic acid as with smoked sheet containing guayule resin.

STEARIC ACID–GUAYULE RESIN REACTION

This extraordinary change in the rate of cure leads to the assumption that the reaction between resin and stearic acid must occur during vulcanization, and that this reaction progresses at a higher rate than the rate of cure, so the rubber mixture is deprived of the effect which stearic acid exerts on vulcanization. But the question still remains whether greater proportions of stearic

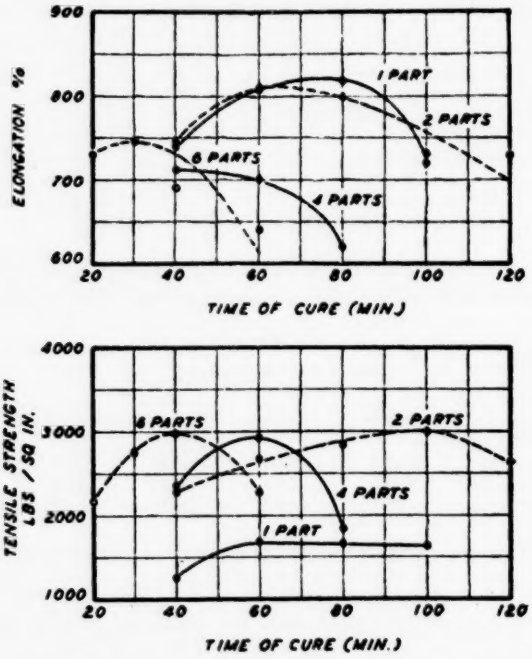

FIG. 1.—Stearic acid in smoked sheet plus guayule resin.

acid are needed for the reaction with the resin alone or whether a surplus of stearic acid is essential to aid vulcanization as well as to react with the resin.

To decide between these two possibilities, it seemed desirable to carry out the reaction between stearic acid and resin before vulcanization. To that end, five parts of resin were preheated with two parts of stearic acid one-half hour and one hour to 65° C. The mixture was then cooled and added to the smoked sheet on the mill. Further compounding was carried out in the regular way. No additional stearic acid was added. The results appear in Figure 2.

It can be seen that heating the resin together with the stearic acid for one-half hour before compounding results is such an increase in the rate of cure that it becomes equal to that of the control. When the resin and the stearic acid were heated for one hour before incorporation into the rubber, no further change in the rate of cure occurred. However, in the latter case the tensile

strength increased above the value obtained from "resinified" mixtures to which six parts of stearic acid had been added on the mill. Since no further increase in the rate of cure is obtained when preheating the resin with twice the percentage of stearic acid, it is evident that not more than two parts of stearic acid are needed to complete the reaction between the fatty acid and the resin. Furthermore these results prove conclusively that no retardation in cure occurs if the resin-stearic acid reaction has been carried out before vulcanization.

That much less stearic acid is needed to obtain optimum tensile strengths if the resin and the stearic acid are preheated together than if they react only during vulcanization finds its explanation in the well-known fact that the

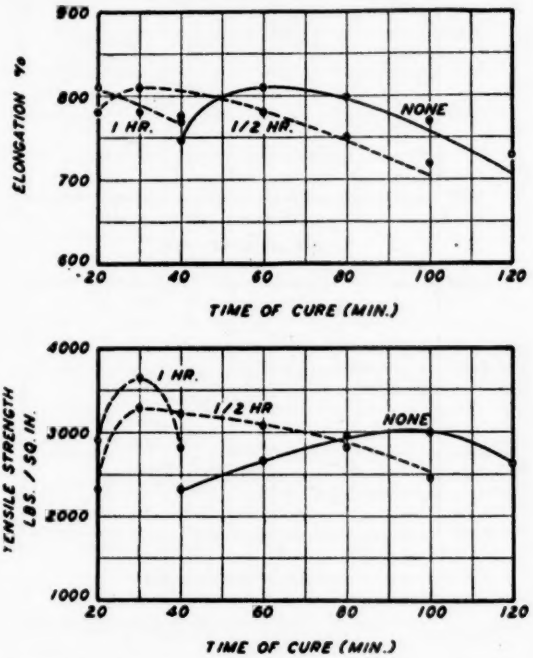

FIG. 2.—Heating guayule resin and stearic acid before compounding.

physical properties of rubber depend to a certain extent on the rate of cure. If vulcanization has to be carried out over a long period of time, thermal degradation of the rubber molecule occurs, with resulting deterioration of physical properties. Where a separate reaction between the resin and the stearic acid is not practical—as in guayule rubber—a higher proportion of stearic acid must be present in the mixture during vulcanization to provide enough surplus so that vulcanization can proceed at the same time as the reaction between stearic acid and resin.

PLASTOGEN, PINE TAR OIL IN PLACE OF GUAYULE RESIN

To overcome criticism that the above results could be explained on the basis that the resin is a diluent of the rubber, mixtures were made in which the

resin was replaced by the same proportions of Plastogen and pine tar oil. Figure 3 shows the physical properties obtained from such mixtures.

It can be seen that Plastogen causes a slight retardation of the cure (as generally known), but does not affect the tensile properties. The increase in elongation was to be expected.

It is interesting, however, to note the similarity of the effect of pine tar oil and guayule resin. An increase of stearic acid in the pine tar oil mixtures

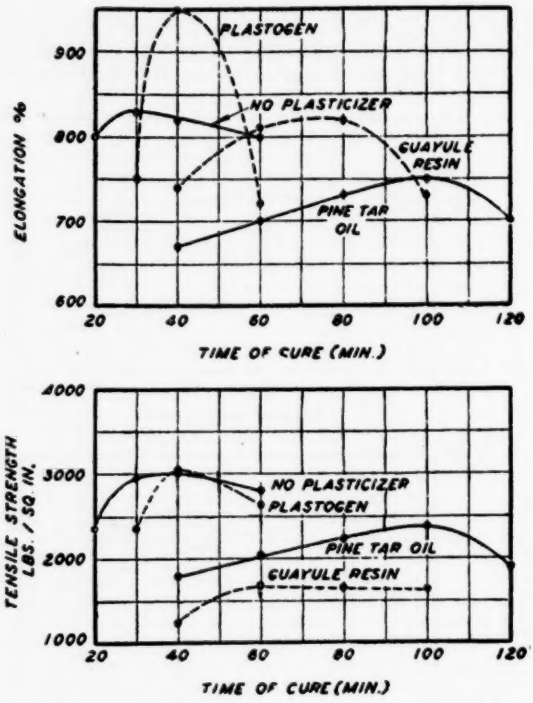

FIG. 3.—Comparison of various plasticizers with guayule resin.

increases the tensile properties and the rate of cure, which is extremely low with small proportions of stearic acid.

In contrast to guayule resin, preheating the pine tar oil with stearic acid does not change the properties of the mixtures.

OTHER FAT ACIDS WITH GUAYULE RESIN

The effect which fat acids exert on rubber mixtures is well known. It therefore seemed of interest to investigate fat acids other than stearic acid with respect to their effect on guayule resin. Palmitic, lauric, and oleic acids (four parts of each) were compounded with smoked sheet containing five parts of guayule resin. Figure 4 shows the physical properties of such mixtures.

It can be seen that lauric and palmitic acids as well as oleic acid result in better tensile strengths and higher elongations than obtained with stearic acid. Mixtures made with lauric acid, moreover, show a plateau effect which for

practical purposes might be more desirable than the higher tensile strengths obtainable with mixtures containing palmitic acid. It is interesting to note that these data follow the work published by Garner, Smith, and Boone[3], who found that in plotting tensile strength *versus* number of carbon atoms of the respective acids a peak in activity can be noticed at 14 carbon atoms.

The high curing rate of the mixtures containing oleic acid can be explained by the greater activity of unsaturated acids.

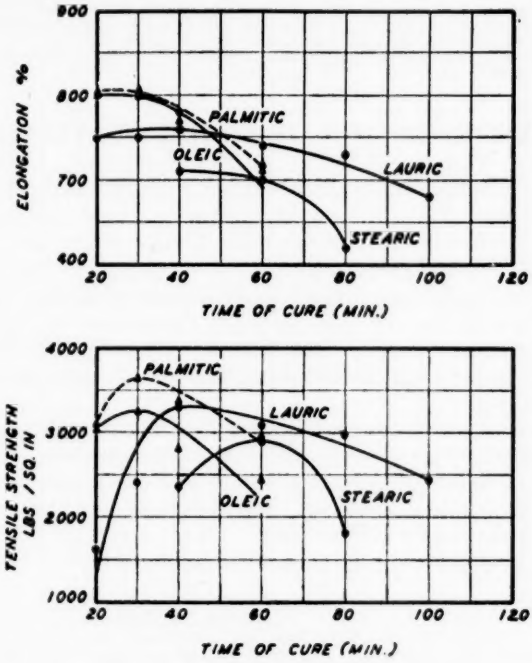

FIG. 4.—Effects of various fatty acids with guayule resin.

If guayule resin is preheated with lauric acid in the same way as described before, the same effect can be noticed as is obtained with stearic acid.

Before an ultimate choice of the most satisfactory fat acid can be made, the question of price, availability and, in particular, its effect on the aging of the vulcanized mixture will have to be taken into consideration.

CONCLUSIONS

The results show conclusively that poor tensile properties occasionally reported for guayule mixtures cannot be ascribed to the guayule rubber hydrocarbon, but are a consequence of the resin still retained in the commercially deresinified product.

These results also explain the injurious effect of the small percentages of guayule resin still present in commercially deresinified guayule rubber as well as the reasons why certain changes in compounding make possible some compensation for these deficiencies. Nevertheless, it is evident that more efficient resin extraction can be considered as the only ideal solution of the problem.

ACKNOWLEDGMENT

The authors are greatly indebted to the Continental Rubber Co. of New York for the underesinified guayule.

REFERENCES

[1] Since it has been impossible to obtain a satisfactory analysis of the very complex guayule resin, the percentages of this resin and of stearic acid used in the rubber mixtures are given merely in parts based on the rubber in the mixtures.

[2] No antioxidant was added so that the number of components and their possible effects on the reactions would be kept at a minimum. All mixtures were kept in cool storage, and were tested in accordance with the time schedule specified by the American Society for Testing Materials; hence the probability of aging effects can be safely disregarded.

[3] Dawson and Porritt, "Rubber, Physical and Chemical Properties", Research Assoc. Brit. Rubber Manufrs., Croydon, 1935, p. 246.

III. DERESINIFICATION OF CRUDE GUAYULE RUBBER *

Resiniferous, commercial guayule rubber contains about 26 per cent of a very tacky resin. The physical properties of crude guayule rubber are extremely poor. On extraction of the resin, however, the physical properties of the remaining rubber hydrocarbon improve greatly. This extraction is carried out commercially with methyl alcohol. About 20 per cent of the resin is removed. Data on the reactions between the remaining resin and certain compounding ingredients during vulcanization, reported in the preceding pages, have shown the importance of a more complete and more efficient removal than hitherto practiced.

For that purpose several solvents were tested in laboratory extraction runs. The solvents tested were chosen for the following reasons:

1. The solvent should be readily available and inexpensive.
2. The solvent should dissolve only the resin, and should remove it quickly without harming the rubber hydrocarbon.
3. The solvent should be easy to recover for reuse.

EXTRACTION WITH VARIOUS SOLVENTS

Methyl alcohol, ethyl alcohol, acetone, 2-nitropropane, 2-furaldehyde, ethyl acetate and nitromethane were tested. Ethyl acetate was found to be unsuitable because it caused excessive swelling of the rubber, and nitromethane was discarded because it was the least effective.

The extractions were carried out in a standard Soxhlet apparatus. The crude guayule was first passed through a rubber mill twice to obtain a thin sheet. All extractions were carried out at the boiling point of each solvent: acetone, 57° C; methyl alcohol, 65° C; ethyl alcohol, 79° C; 2-nitropropane, 120° C; and 2-furaldehyde, 162° C.

The extractions were carried out from one hour to eight hours, and the losses of weight were determined quantitatively at appropriate time intervals. The solvents contained in the samples were removed by keeping the samples in a vacuum desiccator containing a small amount of dry ice. The samples were considered dry when repeated weighing and replacing under vacuum did not change their weights more than 0.0005 gram during a 12-hour period. The loss of weight was then assumed to represent the resin removed from the rubber. Figure 1 shows the losses in weight of 100 grams of crude guayule with different

* Reprinted from the *India Rubber World*, Vol. 107, No. 1, pages 37–39 and 44, April 1943. Part III is based largely on data of W. G. Louden (B.S. Thesis, Mass. Inst. Tech., 1943).

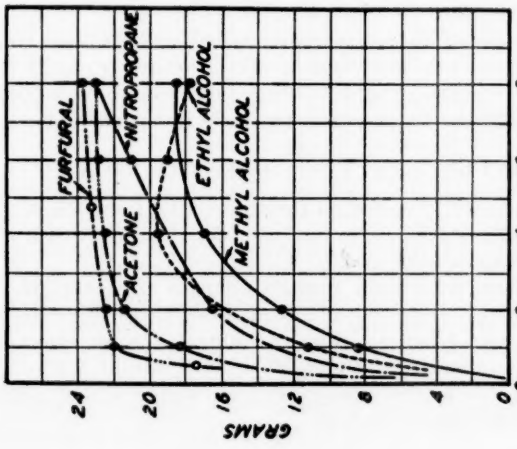

FIG. 1.—Grams of guayule resin extracted with various solvents at boiling point.

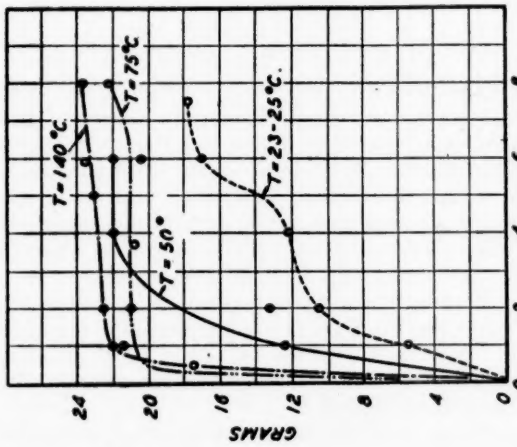

FIG. 2.—Grams of guayule resin extracted with furfural at various temperatures.

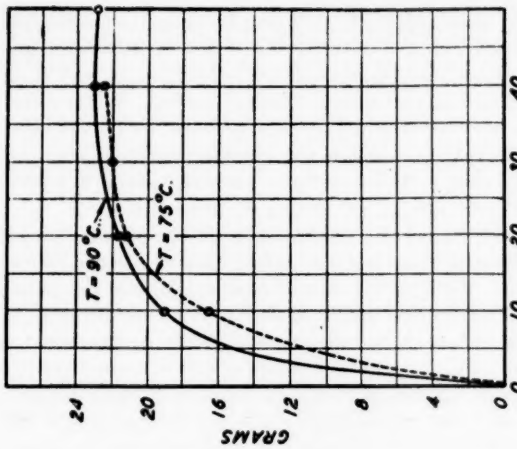

FIG. 3.—Grams of guayule resin extracted with furfural—effect of time of extraction.

solvents and different time intervals. It can be seen that 2-furaldehyde is by far the most efficient solvent. Acetone follows closely in its efficiency at longer time intervals. At short time intervals, as, for example, one hour of extraction, acetone lags considerably behind 2-furaldehyde. Eventually 2-nitropropane (after eight hours' extraction) reaches acetone in its efficiency; whereas ethyl alcohol and methyl alcohol are the least efficient in total extraction as well as rate of extraction. Both of these solvents show a flattening of the extraction curve between 18 and 20 grams of resin removed.

Inasmuch as we are not familiar with the structure of the resin, the assumption is justified that methyl alcohol and ethyl alcohol are capable of dissolving only part of the resin. We are still unable to explain the maximum occurring at four hours' extraction in the ethyl alcohol extraction curve. It should be pointed out, however, that these curves do not really represent the relative extraction powers of the different solvents on a comparative basis, because the extraction temperatures varied with the respective boiling points of the solvents. On the other hand, even such extreme boiling point differences as 100° C occurring between 2-furaldehyde and acetone seem to have little effect on the extraction power of the two solvents.

INFLUENCE OF EXTRACTION TEMPERATURE

As 2-furaldehyde was superior to any other solvent, it was decided to decrease the extraction temperature step by step to ascertain the optimum temperature range, particularly in view of the fact that temperatures as high as the boiling point of 2-furaldehyde might seriously affect the properties of the rubber. For such a study, the Soxhlet extraction apparatus is unsuitable. Therefore the extractions were carried out in a flask equipped with a stirrer and kept in a controlled thermostat set for the desired temperature. Temperatures of 140°, 75°, 50° and 23–25° C were investigated.

Figure 2 shows that there is no advantage in using 2-furaldehyde at its boiling temperature, since the same results in extraction can be obtained at a temperature of 140° C. If extraction is carried out at 75° C, its efficiency must be considered to be superior to that of boiling acetone and, of course, to that of the rest of the solvents investigated.

Figure 2 as well as Figure 1 shows clearly the great advantage of 2-furaldehyde as far as its rate of extraction is concerned. One hour's extraction can be considered sufficient for the removal of the resin up to 22 grams (22 per cent). It should be noted that temperatures below 75° C are not advisable for extraction purposes. It has been observed that, from 75° C upward, 2-furaldehyde seems to exert a slight swelling action on guayule rubber. This swelling tends to facilitate dissolution of the resin in the solvent.

INFLUENCE OF TIME OF EXTRACTION

To investigate the very first part of the time-extraction curves of Figures 1 and 2 in greater detail, experiments were conducted over a range of one hour and only at temperatures of 90° and 75° C.

Figure 3 shows that, within the first 20 minutes of extraction, more than 21 per cent of the resin is removed and that, from approximately 40 minutes on, the amount of resin extracted does no longer change appreciably with time. Although at temperatures above 90° C, the rate of extraction may be somewhat higher, it was feared that such high temperatures might cause a breakdown of the rubber hydrocarbon.

To prove this point, about 500 grams of crude guayule were extracted in boiling 2-furaldehyde for one hour; the solvent remaining in the rubber was removed by steam distillation. The rubber was then resheeted, an antioxidant was added immediately, and the rubber sheet was dried in air. The dry sheet was then compounded on a warm mill (140° F) according to the following standard formula: rubber 100, sulfur 3, mercaptobenzothiazole, 1 stearic acid 1, zinc oxide 5.

Since previous experiments on guayule rubber had shown the necessity of increased proportions of stearic acid, a second mixture was prepared which was identical with the above, except that it contained four parts of stearic acid. Two blank mixtures of exactly the same formulation, but with the commercially deresinified guayule containing 6 per cent resin, were also prepared. All mixtures were vulcanized at 270° F. No change in the rate of cure could be observed between the two mixtures prepared from guayule extracted with 2-furaldehyde and the two mixtures prepared from commercially deresinified guayule. Table 1 shows the physical properties of the four mixtures at their optimum cures.

TABLE 1

Compound containing	Solvent used for extraction	Tensile strength (lbs. per sq. in.)	Elongation (percentage)
1 part stearic acid	2-furaldehyde	3500	710
4 parts stearic acid	2-furaldehyde	3900	660
1 part stearic acid	Commercially deresinified (methyl alcohol)	2350	790
4 parts stearic acid	Commercially deresinified (methyl alcohol)	3400	700

Contrary to what might have been expected, it can be clearly seen that the temperature of extraction with 2-furaldehyde (162° C), at least within the time limit investigated, had no ill effects on the rubber hydrocarbon. Furthermore, the more complete removal of the resin which can be obtained by this method improves the physical properties. Tensile strength values are obtained with one part of stearic acid which are far superior to those obtained from the same mixture prepared from commercially deresinified guayule. Also, the ultimate tensile strengths obtained with four parts of stearic acid and 2-furaldehyde extracted guayule are superior to those obtained from the same mixture prepared from commercially deresinified guayule.

INFLUENCE OF ANTIOXIDANT

It should be pointed out that guayule rubber seems extremely sensitive to the influence of antioxidants. Commercially deresinfiied guayule, which has been used in the present and all previous investigations, contains antioxidant. Experiments on the purification of guayule rubber by precipitation of the rubber hydrocarbon from benzene solution with ethyl alcohol have shown that the pure rubber hydrocarbon obtained in this way is extremely unstable, and reverts to a soft flowing sticky mass if stored in contact with light and air. Thus it seems advisable to add an antioxidant as soon as the resin is completely extracted, or, if the antioxidant is insoluble in the solvent used for extraction, it might preferably be added before extraction is started.

EFFECT OF EXTRACTION ON THE MOLECULAR WEIGHT

To determine further the effect of extraction on the rubber hydrocarbon, determinations of its molecular weight were carried out. Although the determinations of the physical properties of guayule rubber extracted for one hour at the boiling point of 2-furaldehyde have indicated that no marked change in the rubber hydrocarbon could have occurred, it was considered advisable to extend this investigation to longer times of extraction as well as to the solvents used.

Guayule rubber was extracted in a Soxhlet apparatus at the boiling temperatures of the various solvents. At certain time intervals of extraction, samples were removed, dried to constant weight, and dissolved in benzene. The solutions were precipitated in ethyl alcohol, and the vacuum-dried rubber was redissolved in benzene. After the second alcohol precipitation, benzene solutions of various concentrations were prepared for the determination of relative viscosities, and the modified Staudinger formula $M = \frac{\log \eta}{K_{cm}C}$ was used. Since it had been shown that guayule is subject to quick breakdown on the mill, and since all the samples had been passed through the mill twice to obtain samples suitable for extraction, it seemed more reasonable to use Staudinger's constant $K = 1 \times 10^{-4}$ rather than the one suggested by Kemp and Peters[1].

Figure 4 shows the influence of the time of extraction on the molecular weight with various solvents. Extraction with methyl alcohol up to two hours does not seem to affect the molecular weight. From then on a steady decrease in the molecular weight can be noticed until, after eight hours' extraction, it drops to 88 per cent of its original value; whereas the resin extracted after six hours does not amount to more than 17 per cent and after eight hours to 18.5 per cent. The molecular weight of guayule rubber extracted with 2-nitropropane drops rapidly in the second hour of extraction to 73 per cent of the original value and then shows practically no further change. This drop in the molecular weight occurs at a time of extraction when only slightly more than 16 per cent of the resin has been extracted. The curve representing the progress of extraction with 2-furaldehyde shows a drop in the molecular weights of only 5 per cent after one hour of extraction and 33 per cent after eight hours. The latter is the lowest molecular weight recorded in this series. However, after one hour of extraction with 2-furaldehyde, 23 per cent of resin has been removed, and further extraction is unnecessary. The physical data of the mixtures show that the 5 per cent drop in molecular weight does not affect seriously the tensile strength of the rubber.

But it should be pointed out that the above determinations of the molecular weights may not represent the actual molecular weights. As mentioned previously, a portion of the resin seems to be insoluble in alcohol, and therefore may still be present in the reprecipitated rubber. Thus we may expect the molecular weight of pure guayule rubber to be somewhat higher than recorded.

A comparison of molecular weights determined for guayule with those of *Hevea* rubber, coupled with the fact that the tensile strengths of pure-gum mixtures of *Hevea* and guayule are practically the same, seems to indicate that the chain length of the polymer alone is not responsible for tensile strength.

It must be kept in mind, however, that such molecular weight determinations and data represent the average distribution of the various chain-lengths present in the particular rubber. It is quite possible that the guayule hydrocarbon, although having a certain number of chains of possibly the same length

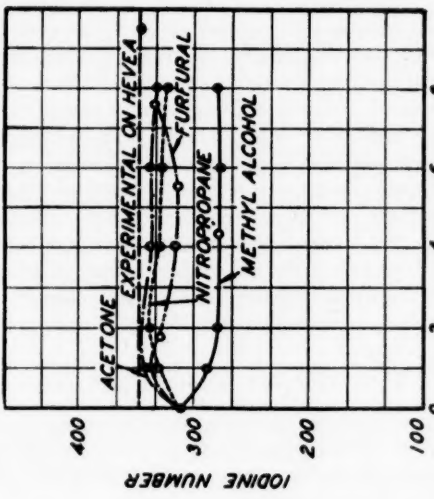

FIG. 5.—Effect of time of extraction with different solvents on unsaturations.

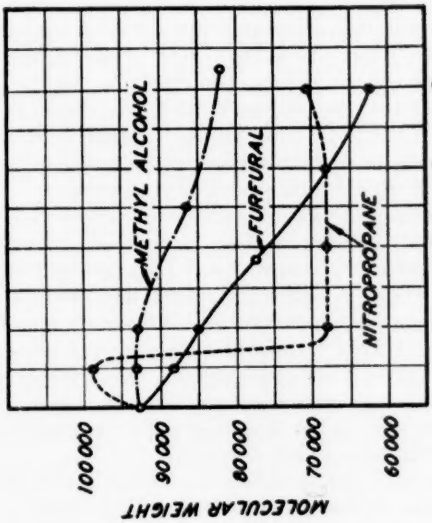

FIG. 4.—Effect of time of extracting on the molecular weight with different solvent.

as *Hevea* rubber, may possess an average distribution of chain size entirely different from that of *Hevea* rubber. The work of Hauser and Brown[2] on the determination of the loss of unsaturation during vulcanization seems to point to the assumption that combination of sulfur and the resultant comparatively small loss of unsaturation cannot be considered as the sole reaction during vulcanization and the only one responsible for the tremendous changes in the properties of the rubber during and after that period. It is conceivable that, during vulcanization, certain physical changes may occur which cannot be ascertained by chemical analysis. This would explain why the molecular weight of the polymer alone may not—within certain limits—govern the tensile properties of the vulcanized product, provided, of course, that polymers are compared whose chemical and physical structure are essentially the same.

The decrease in molecular weight during extraction can be explained by a breakdown of molecules because of the prolonged action of heat, although the possibility of oxidation occurring during that period cannot be disregarded completely. It is, however, extremely difficult to prove this point experimentally.

DETERMINATION OF UNSATURATION

Finally it was thought of interest to compare the iodine number of guayule rubber with that of *Hevea*, and to ascertain, if possible, whether extraction exerts any influence on unsaturation. The method used for this purpose was discussed in detail by Hauser and Brown[2].

Figure 5 shows the effect of various solvents, as well as the effect of the time of extraction on the unsaturation of guayule rubber.

The initial rise in the unsaturation with all solvents except methyl alcohol can be explained by the removal of the greater part of the resin during the first hour of extraction. The assumption that part of the resin is insoluble in alcohol, and hence is not removed during purification, seems justified. This point is further substantiated by the fact that the maximum unsaturation occurs in each case when the extraction curves (Figure 1) flatten. Although prolonged extraction results in a great change in the molecular weight for most solvents investigated, the unsaturation is hardly affected.

The curve of unsaturation of guayule rubber extracted with methyl alcohol shows the smallest iodine numbers. This again can be explained on the assumption that methyl alcohol dissolves only part of the resin.

There remains the question whether the resin itself affects the unsaturation of guayule rubber at elevated temperatures. Therefore resiniferous guayule was placed into an oven at 92° C, samples were removed at certain intervals, and their unsaturation values were determined. No change in unsaturation could be detected. The unsaturation of the extracted guayule resin corresponds to an iodine number of 117. That the iodine number does not change over a long period of extraction is not surprising.

Two possibilities of breakdown of the rubber chains can be envisaged. The chain either can split close to the ends, leaving a long chain with one or two short residual chains, or it can split near the middle, resulting in two still comparatively long chains. In the former case, the change in the molecular weight as determined should be small in comparison with the latter. The change in unsaturation is more pronounced in the former case. The experimental methods applied in this investigation do not, unfortunately, make it possible to say whether oxidation or simple thermal breakdown of the chains is responsible for the drop in molecular weight recorded.

CONCLUSION

It has been shown that different solvents used in the extraction of the resin from crude guayule exhibit different time-temperature relations.

Of all the solvents tested, 2-furaldehyde was found to be the most efficient solvent for its speed and for the amount of resin extracted. It does not affect adversely the properties of the hydrocarbon.

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[1] Kemp and Peters, *Ind. Eng. Chem.* **33**, 1391 (1941).
[2] Hauser and Brown, *Ind. Eng. Chem.* **30**, 1291 (1938); **31**, 1225 (1939).

THE COMPOUNDING OF GUAYULE RUBBERS

EFFECT OF ACCELERATOR-CURING AGENT COMBINATIONS*

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PURPOSE OF INVESTIGATION

Literature on the compounding of guayule rubber is very scarce. The authors have found only two papers which give any information on this subject, one by Spence and Boone[1], the other by Doering[2]. The former paper deals specifically with the question of the quality of the rubber derived from the guayule shrub by suitable treatment, guarding against deterioration. The latter paper is concerned with the use of guayule rubber in tires and tubes. No systematic study of the effect of compounding ingredients is presented in either paper.

TYPES OF GUAYULE RUBBER

Three types of guayule rubber are available: domestic deresinated, domestic resiniferous, and Mexican resiniferous[3]. Deresinated guayule rubber is obtained from the domestic resiniferous product by prolonged extraction with acetone or similar solvent, followed by drying. Both domestic products are available in limited quantities at the present time because of restricted planting, but the Mexican product is more readily procurable, since it is obtained from wild growth.

The domestic products employed in this testing program were supplied by the experimental plant of the Intercontinental Rubber Co., Salinas, California; the Mexican product was one of the regular brands being supplied to the trade.

The guayule rubbers are characterized by comparatively high contents of acetone-soluble substances and fibrous material. Deresinated guayule rubber, of course, contains less acetone-soluble substances than the other guayule rubbers, but more than does *Hevea* rubber. Table I gives the percentages of

TABLE I

ACETONE-SOLUBLE SUBSTANCES AND FIBROUS MATERIAL IN *Hevea* AND GUAYULE RUBBERS

	Acetone-soluble substances (percentage)	Fibrous material (percentage)
Prime smoked sheet	3.3	0.0
Domestic resiniferous guayule rubber	15.6	0.31
Domestic deresinated guayule rubber	6.1	0.13
Mexican resiniferous guayule rubber	25.9	0.20

* Reprinted from the *India Rubber World*, Vol. 105, No. 6, pages 565–569, March 1, 1942.

these substances in the guayule rubbers and *Hevea* rubber (prime smoked sheet) used in the compounding tests. It will be noted that the resin content of the Mexican guayule rubber is considerably higher than that of the domestic product.

FORMULAS

The basic formula selected for the compounding tests is believed to be representative of a medium-hard, mechanical goods stock, except that no antioxidant is included. The antioxidant was left out of the formula to appraise better the inherent resistance to aging of the guayule rubber stocks and the effect of accelerators on the resistance to aging. The basic formula is given below.

Rubber	100
Semi-reënforcing carbon black (Pelletex)	50
Zinc oxide	5
Stearic acid	2

Eight accelerator-curing agent combinations were chosen as typical of modern practice in the compounding of *Hevea* rubber stocks. The accelerators included representatives of all popular types, and the curing agents included normal sulfur, low sulfur, and tetramethylthiuram disulfide with tellurium. The combinations and identifying numbers are listed in Table II. It should

TABLE II

ACCELERATOR-CURING AGENT COMBINATIONS

Combination No.	Accelerator	Amount per 100 rubber	Curing agent	Amount per 100 rubber
1	Mercaptobenzothiazole	0.8	Sulfur	2.5
2	Dibenzothiazyl disulfide	0.8	Sulfur	2.5
	Zinc dimethyldithiocarbamate	0.1		
3	2-Mercaptothiazoline	0.5	Sulfur	2.75
	Butyraldehydeaniline condensation product	0.1		
4	Butyraldehydemonobutylamine condensation product	0.5	Sulfur	2.5
5	Di-*o*-tolylguanidine	1.0	Sulfur	3.0
6	Tetramethylthiuram monosulfide	0.2	Sulfur	2.0
7	Mercaptobenzothiazole	0.5	Sulfur	0.75
	Dibenzothiazyl disulfide	0.5		
	Tetramethylthiuram disulfide	0.5		
8	Mercaptobenzothiazole	1.0	Tetramethylthiuram disulfide	3.0
			Tellurium	0.5

be pointed out that mercaptobenzothiazole, when used with tetramethylthiuram disulfide and tellurium in combination No. 8, really acts as a retarder instead of an accelerator.

Master batches were compounded from smoked sheet, deresinated guayule rubber, domestic guayule rubber, and Mexican guayule rubber, using the basic formula given above. The master batches were mixed on a 40-inch mill. Eight stocks were then compounded from each master batch, using one of the eight accelerator-curing agent combinations in each stock. The stocks were mixed on a 12-inch laboratory mill. All mixing operations were performed strictly in accordance with the standard methods of the A. S. T. M.[4]

The authors acknowledge that the sulfur ratios employed may not be sufficient for the guayule rubbers because of their high resin content. The effect of sulfur ratio on the physical properties of the guayule stocks will be the subject of further study.

CURING

Since it was proposed to carry out a comprehensive testing program on thirty-two stocks, it was not possible to perform all tests on each stock without unduly delaying the investigation. The time of cure at 287° F for each stock, which gave optimum tensile strength, was selected as the best cure for testing. Since tensile strength measurements were made on sheets 0.07 to 0.08 inch thick, thicker test-specimens were given a longer cure; for example, the ¼-inch thick flexing specimens were cured three minutes longer, the ½-inch thick compression-set specimens were cured five minutes longer, and the one-inch thick rebound specimens were cured 15 minutes longer.

The times of cure for optimum tensile strength are given in Table III.

TABLE III

TIME OF CURE 287° F FOR OPTIMUM TENSILE STRENGTH

Accelerator-curing agent combination No.	Type of rubber	Time of cure at 287° F for optimum tensile strength (minutes)	Accelerator-curing agent combination No.	Type of rubber	Time of cure at 287° F for optimum tensile strength (minutes)
1	SS	20	5	SS	30
	DG	20		DG	40
	RG	20		RG	30
	MG	30		MG	40
2	SS	5	6	SS	5
	DG	10		DG	10
	RG	10		RG	10
	MG	10		MG	10
3	SS	30	7	SS	5
	DG	40		DG	10
	RG	30		RG	10
	MG	40		MG	10
4	SS	30	8	SS	20
	DG	30		DG	30
	RG	30		RG	20
	MG	30		MG	30

In this table and in the charted data the following abbreviations are employed to designate the type of rubber in the stock:

Prime smoked sheet	SS
Domestic deresinated guayule	DG
Domestic resiniferous guayule	RG
Mexican resiniferous guayule	MG

It will be noted in Table III that the general tendency was for the smoked sheet stocks to cure the fastest, followed in order by the domestic guayule stocks, the deresinated stocks, and the Mexican guayule stocks.

PROGRAM OF TESTS

The following program of tests was selected as of particular interest to manufacturers of mechanical goods:

Tests on unvulcanized stocks.

1. Plasticity at 212° F—initial and after two hours at 212° F.

Tests on vulcanized stocks.

1. Shore hardness—initial and after aging for 24 hours in oxygen bomb.
2. Tensile strength—initial, after aging for 24 hours in oxygen bomb, and after immersion for two months in distilled water.
3. Ultimate elongation.
4. Modulus at 300% elongation.
5. Permanent set.
6. Tear resistance—initial and after aging for 24 hours in oxygen bomb.
7. Rebound.
8. Resistance to flex cracking.
9. Compression set.

The oxygen bomb aging was performed at 158° F under 300-pounds-per-square-inch oxygen pressure. Details on the other tests are given below.

RESULTS OF TESTS

Processing.—Processing details are always of major importance to the manufacturer. The behavior of the guayule rubbers during the mixing of the master batches on a 40-inch mill is recorded in the following paragraphs.

Deresinated guayule rubber behaved like prebroken-down smoked sheet. The master batch was mixed without any difficulty. The finished master batch had about as much nerve as double-broken-down smoked sheet.

Domestic guayule rubber broke down quite easily. The only difficulty noticed during the mixing operation was that the rubber had a tendency to break away from the front roll after most of the black had been added. The finished master batch possessed little nerve; it was soft and fairly tacky, but showed no inclination to stick to the back roll when sheeted off.

Mexican guayule rubber was extremely soft and tacky. It handled satisfactorily on a cold mill, but on a warm mill it stuck badly to the back roll. It also stuck to the operator's hands, mill knife, etc. The finished master batch stuck to galvanized steel, so it was necessary to use liberal quantities of soapstone or zinc stearate on the metal surface when sheeting. Even the cured stock compounded from this rubber was quite tacky.

Plasticity.—The purpose of the plasticity tests was to determine the relative stiffness of the stocks and their relative rates of set-up or scorching. For this purpose a Scott pedestal-type plastometer, with total weight of 10 pounds on the upper platen, was employed. Steam was blown through the hollow cavities in the platens of the plastometer to obtain a temperature of 212° F on the surface of the platens. Small sheets of the stocks were plied to a thickness of 0.3–0.4 inch to make specimens. The initial plasticity was determined by inserting a specimen in the plastometer and lowering the upper platen until the rubber was compressed to a thickness of 0.250 inch between the upper platen and the pedestal. After a warming period of ten minutes, the upper platen was released. The thickness of the specimen after three minutes was taken as a measure of the toughness or stiffness of the stock.

To determine the rate of set-up of the stocks, specimens were placed in an air oven maintained at 212° F. At the end of two hours the specimens were removed, and their plasticity determined by the procedure described above.

The results of the plasticity tests are given in Figure 1[5].

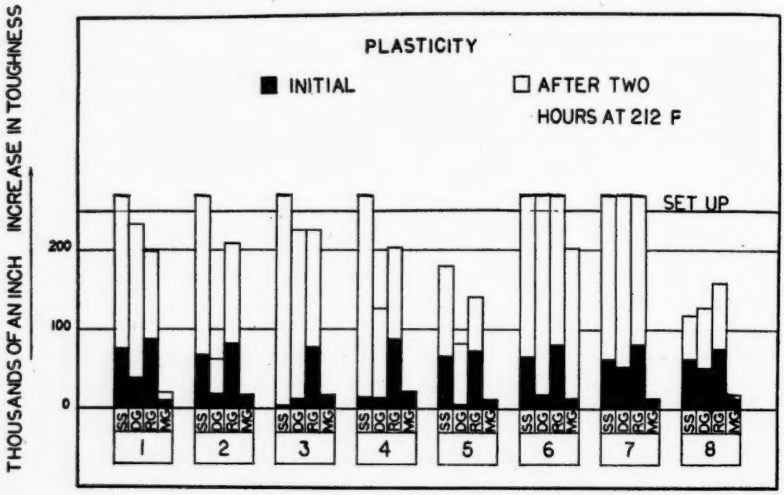

FIG. 1.

The charted plasticity data indicate that the smoked sheet stocks are more scorchy than any of the guayule stocks and that the deresinated and domestic guayule stocks are more scorchy than similar Mexican guayule stocks. It is interesting that the relative increase in toughness of the deresinated and domestic guayule stocks in the scorch test parallels the increase in toughness of

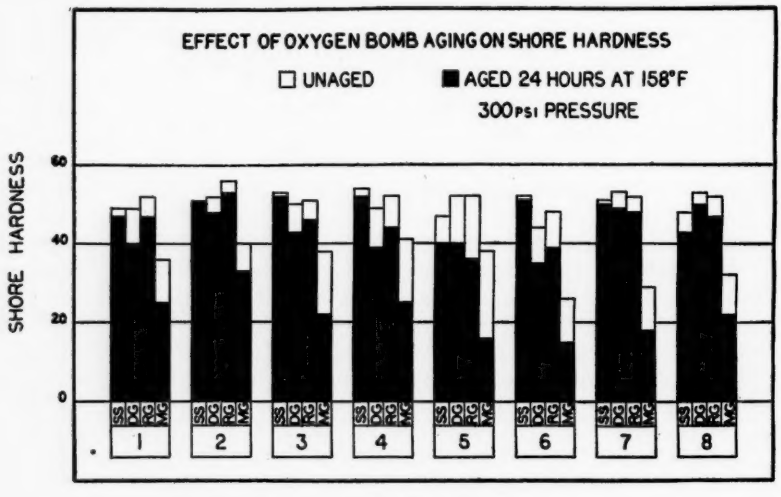

FIG. 2.

similar smoked sheet stocks in most cases, thus proving that these rubbers are affected in a like manner by a given A-C combination.

Perhaps the most significant information to be gained from the chart is the pronounced initial toughness of the domestic guayule stocks. Whereas the deresinated guayule stocks and Mexican guayule stocks might be troublesome to process because of excessive softness, the domestic guayule stocks should process almost as well as similar smoked sheet stocks.

Shore hardness.—The Shore hardnesses of the vulcanized stocks before and after aging in the oxygen bomb are given in Figure 2. The hardness measurements were made on specimens ½ inch thick.

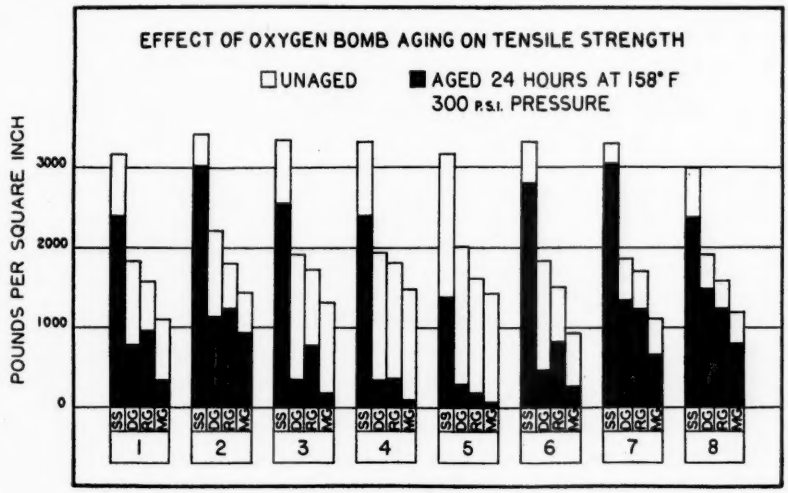

FIG. 3.

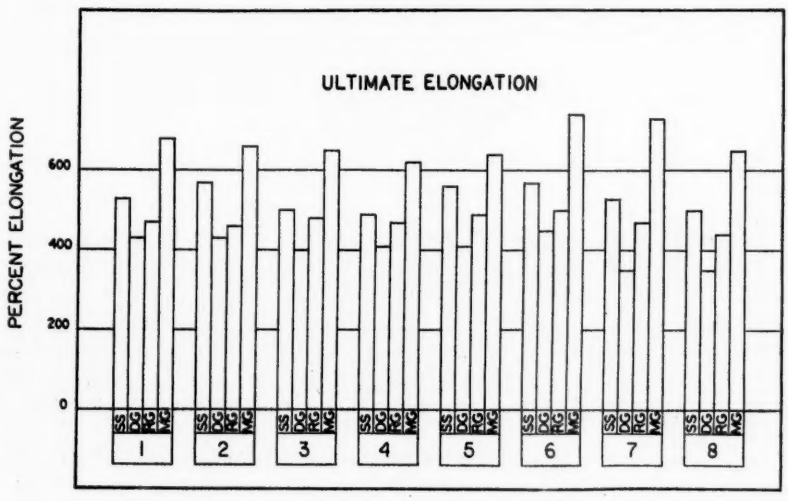

FIG. 4.

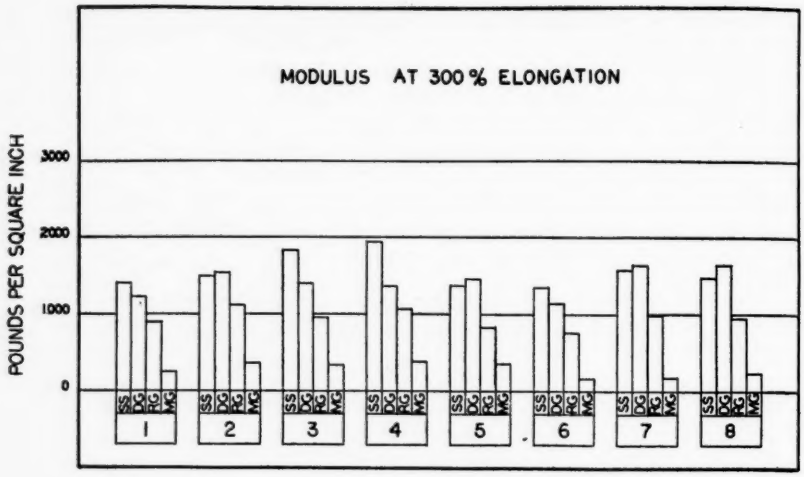

FIG. 5.

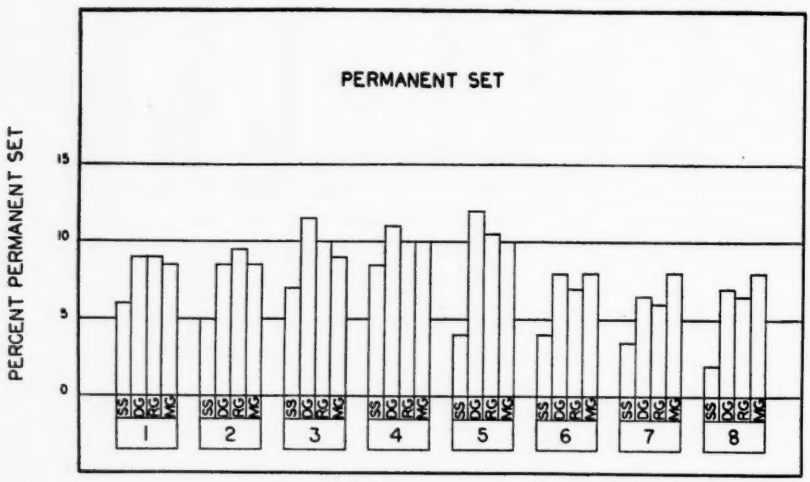

FIG. 6.

The deresinated and domestic guayule stocks in most cases equal, or even exceed, the similar smoked sheet stocks in hardness. The Mexican guayule stocks, on the other hand, are all softer than the others, and they are more affected by the A-C combination used. The smoked sheet stocks generally resist aging better than any of the guayule stocks, and the deresinated and domestic guayule stocks are better than the Mexican guayule stocks in this respect. A-C combination No. 2 provides the greatest stability against aging for all the rubbers.

Tensile properties.—The tensile properties: tensile strength, ultimate elongation, modulus at 300 per cent elongation, and permanent set, are charted in Figures 3, 4, 5, and 6, respectively.

The tensile strengths of the deresinated guayule stocks average about two-thirds the tensile strengths of similar smoked sheet stocks. The tensile strengths of the domestic guayule stocks are 200 to 400 pounds lower, and the Mexican guayule stocks are 500 to 900 pounds lower than the tensile strengths of the deresinated guayule stocks. A-C combination No. 2 produced the highest tensile strengths for the smoked sheet and deresinated guayule stocks; this combination and combination No. 4 produced the highest tensile strengths for the domestic and Mexican guayule stocks.

The Mexican guayule stocks exhibited the highest elongations at break, followed in order by the smoked sheet, domestic and deresinated guayule stocks.

The moduli at 300 per cent were considerably affected by the A-C combinations. Combinations Nos. 3 and 4 produced the highest moduli for smoked sheet, but, surprisingly, the low-sulfur and nonsulfur combinations Nos. 7 and 8, respectively, produced the highest moduli for deresinated guayule rubber. Combinations Nos. 2 and 4 yielded the highest moduli for the domestic and Mexican guayule rubbers.

The permanent set measurements were made at 300 per cent elongation, according to the standard method of the A. S. T. M.[6] The smoked-sheet stocks had lower permanent set than the corresponding guayule stocks. The permanent sets of the guayule stocks were about the same for a given A-C combination, not differing one from another by more than 2 per cent (actual value). The low-sulfur and nonsulfur stocks of all the rubbers, A-C combinations Nos. 7 and 8 gave the lowest permanent sets.

Effect of aging in oxygen bomb.—The tensile strengths after aging for 24 hours in the oxygen bomb are given in Figure 3, together with the initial values. The percentage drop in tensile strength of the guayule stocks is much greater than with the corresponding smoked sheet stocks, although the actual amount of drop is less in certain cases. Of the guayule stocks, the Mexican generally suffered the greatest deterioration, and the domestic the least. One normal sulfur formula, A-C combination No. 2, and the low-sulfur and nonsulfur formulas, A-C combinations Nos. 7 and 8, produce the best aging stocks for any of the four rubbers.

Effect of immersion in water.—Dumbbell specimens were immersed in distilled water, maintained at a temperature of 85° F, for two months. They were tested for tensile properties immediately after removal from the water. It was thought that the presence of fibrous material might bring about the deterioration of the guayule stocks, due to the rapid diffusion of the water into the interior of the rubbers.

The tensile strengths and elongations of all the stocks were very little changed by the immersion except in the case of the Mexican guayule stock containing A-C combination No. 7; the tensile strength of this stock dropped 16 per cent.

The moduli at 300 per cent elongation were more affected in every instance, particularly in the case of the guayule stocks. For example, the modulus of the domestic guayule stock containing A-C combination No. 4 dropped 25 per cent, although the tensile strength decreased only 2 per cent and the ultimate elongation increased 6 per cent.

Tear resistance.—The tear resistances before and after aging for 24 hours in the oxygen bomb are given in Figure 7. These tear resistances were measured according to the proposed method of the A. S. T. M.[7], with the modifica-

tion proposed by Poules[8]. Poules found that more uniform results are obtained with one cut midway between the ends of the test-piece than is the case if the usual five cuts are made.

It will be noted in Figure 7 that domestic guayule stocks have the best initial tear rsistances among the guayule stocks. With two exceptions, the

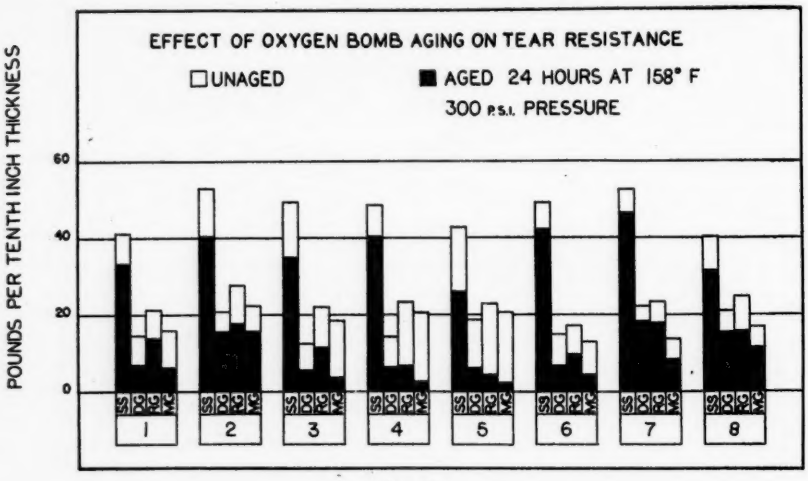

FIG. 7.

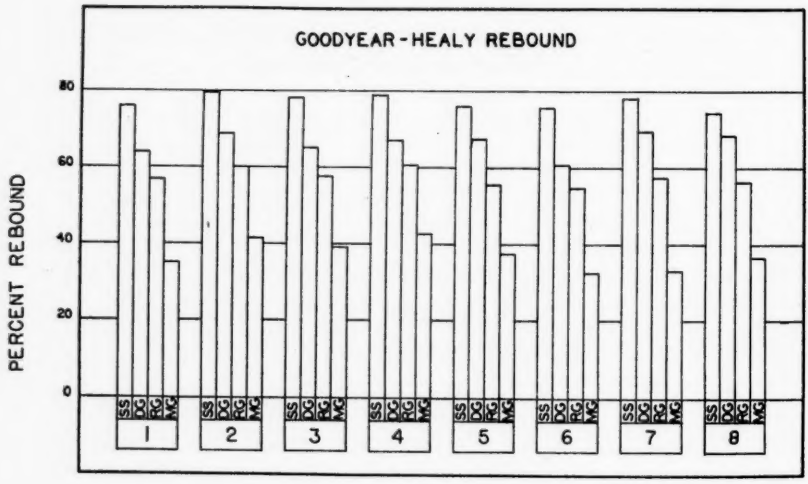

FIG. 8.

same can be said of the tear resistances after aging. However, the tear resistances of the smoked sheet stocks are about 100 per cent greater than those of the corresponding domestic guayule stocks.

The best tear resistances after aging of the guayule stocks were obtained with the normal-sulfur formula, A-C combination No. 2, the low-sulfur formula, A-C combination No. 7, and the nonsulfur formula, A-C combination No. 8.

Rebound.—Rebound or resilience was measured with the Goodyear Healy rebound pendulum. An angle of drop of 20 degrees and a test-piece 1 × 1 × 2 inches were utilized. The data are charted in Figure 8.

The data show that the rebounds of the deresinated guayule stocks and domestic guayule stocks approach those of similar smoked sheet stocks; the former guayule stocks are the better. The Mexican guayule stocks have rebounds equal to approximately one-half the rebounds of similar smoked sheet stocks. The normal-sulfur formulas, A-C combinations Nos. 2 and 4, give the highest rebounds for the four rubbers.

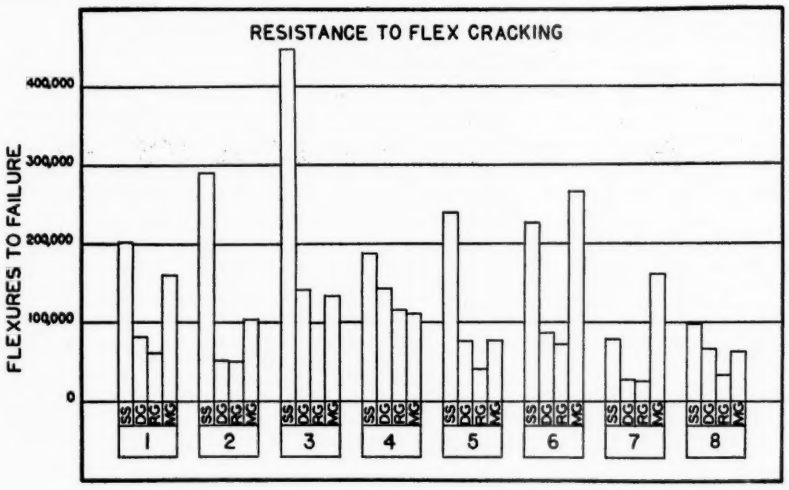

FIG. 9.

Resistance to flex-cracking.—The resistance to flex-cracking due to bending was determined on the de Mattia tester. The basis for comparison was the number of flexures required to produce a crack through the specimen at the circular groove. The results are given in Figure 9.

Surprising results were obtained from the flexing tests. By far the best stock was the smoked sheet stock containing A-C combination No. 3, but exceptionally good resistance to flex-cracking was exhibited by the Mexican guayule stock containing A-C combination No. 6. The latter stock was even somewhat better than the similar smoked sheet stock, and very much better than the similar deresinated and domestic guayule stocks. With the exception of the stocks containing A-C combinations Nos. 3 and 4, the deresinated and domestic guayule stocks had poor resistances to flex cracking.

Compression set.—The results of the compression set tests under constant load are given in Figure 10. The procedure recommended by the A. S. T. M. was used[9].

It is generally recognized that the compression set of a vulcanized rubber stock is affected greatly by state of cure. The cure for optimum tensile strength is usually not the cure for minimum compression set; consequently the values given in Figure 10 are not the best that can be obtained with the respective stocks. Nevertheless, these values are considered to be suitable for the purpose of comparison.

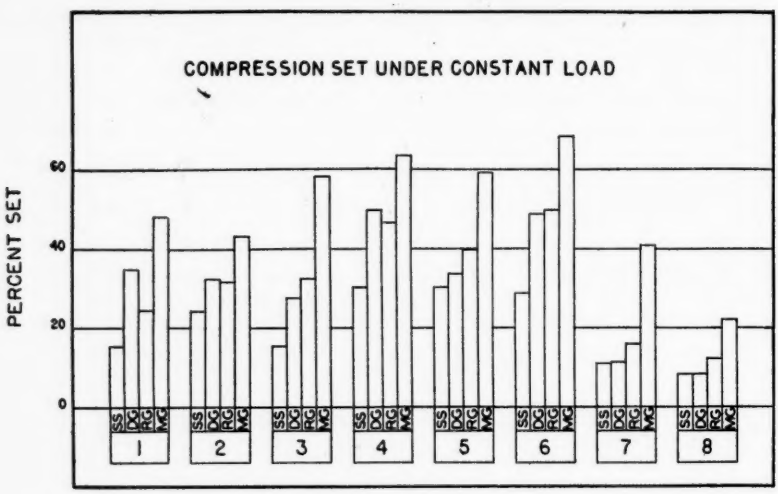

FIG. 10.

It will be observed in Figure 10 that the smoked sheet stocks have the lowest compression sets except with A-C combination No. 8, where the compression set of the deresinated guayule stock equals that of the similar smoked sheet stock. The lowest compression sets for all the rubbers are obtained with the low-sulfur and nonsulfur formulas.

CONCLUSIONS

The accelerator-curing agent combinations in most cases have the same effect on the three guayule rubbers as they have on smoked sheet. No accelerator-curing agent combination produces smoked-sheet stocks or guayule stocks excelling in every property; each rubber must be specially compounded for the purpose in mind.

The authors conclude from the test data reported above that stocks prepared from domestic deresinated guayule rubber do not show sufficient advantages over similar stocks prepared from domestic resiniferous guayule rubber to justify the extra expense involved in the preparation of the former rubber. On the other hand, stocks prepared from Mexican resiniferous guayule rubber are definitely of poorer quality than similar stocks prepared from the domestic products.

ACKNOWLEDGMENT

The authors wish to acknowledge the coöperation of Irwin H. Whitthorne in this investigation.

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[4] Standard methods of sample preparation for physical testing of rubber products: A. S. T. M. Designation D15–39.
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THE COMPOUNDING OF GUAYULE RUBBERS

EFFECT OF VARIOUS FACTORS ON PHYSICAL PROPERTIES *

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This paper is the third in a series of reports on the compounding of guayule rubbers. The previous papers[1] dealt with the effects of accelerator-curing agent combinations on the properties of stocks prepared from *Hevea* rubber and three guayule rubbers, each of different resin content. The purpose of the present paper is mainly to show data on the effects of rubber breakdown and temperature of cure on the tensile strengths of guayule stocks and similar *Hevea* stocks, and to present the results of a study of the effects engendered in guayule stocks and similar *Hevea* stocks by variation in their stearic acid content.

Hauser and Le Beau[2] recently published an interesting paper describing experiments on guayule rubber. The experiments were conducted to determine the effects of breakdown temperature, curing temperature, and stearic acid content on the tensile strength-time of cure relation of a pure-gum stock prepared from commercial deresinated guayule rubber. These investigators concluded that "guayule rubber may not be processed, compounded, or vulcanized by standard *Hevea* rubber methods if maximum physical properties are desired, and that with appropriate compounds, commercially deresinified guayule can result in cured stocks which are equivalent in their physical properties to those which are prepared from *Hevea* rubber".

Inasmuch all rubber manufacturers wish to obtain maximum physical properties from crude rubber, it is important to evaluate carefully the accepted methods for processing and vulcanizing *Hevea* rubber with regard to their applicability to guayule rubber. Accordingly the authors have repeated several of the experiments of Hauser and Le Beau. In some cases very similar recipes were used; in other cases recipes devised by the authors were used. In every case similar smoked sheet stocks were tested for comparison.

EFFECT OF MILLING TEMPERATURE

The mill-roll temperatures for the breakdown and mixing of *Hevea* stocks are generally kept as low as possible in factory practice, primarily to avoid scorching, and secondarily to reduce the nerve of the rubber. The reduction in physical properties which might result from a low milling temperature is generally considered to be negligible.

A 6 × 13-inch laboratory mill with a friction ratio of 1.4 was employed for finding the effect of mill temperatures in this investigation. The authors recognize that this mill is a far cry from large factory mills, but it is believed

* Reprinted from the *India Rubber World*, Vol. 107, No. 5, pages 463–467, February 1943.

that the temperature effect will, if anything, be more pronounced with this mill than with a larger machine. The temperatures of the rolls on the laboratory mill were determined with a Cambridge surface pyrometer at the start and finish of the batches. The temperature of the rubber was determined by wrapping the stock around a thermocouple immediately after sheeting off.

Recipe No. 1 in Table I was employed for the temperature tests. This recipe is believed to be representative of a medium-hard mechanical goods stock. The deresinated Mexican guayule rubber was prepared by extracting

TABLE I

RECIPES TESTED

	No. 1	No. 2	No. 3	No. 4
Rubber	100.0	100.0	100.0	100.0
Pelletex	50.0	...	...	50.0
Zinc oxide	5.0	5.0	5.0	5.0
Stearic acid	2.0	variable	variable	variable
Mercaptobenzothiazole	...	1.0	...	...
Benzothiazyl disulfide	0.8	...	0.8	0.8
Zinc dimethyldithiocarbamate	0.1	...	0.1	0.1
Sulfur	2.5	2.5	2.5	2.5

the resiniferous rubber with acetone, then drying the extracted rubber at 160° F in a vacuum. The deresinated rubber contained 5.6 per cent acetone-soluble substances and 0.06 per cent fibrous substances (caught on a 100-mesh screen). The batch weight of each stock was 641.6 grams.

The total mixing time was 25 minutes, including a two-minute breakdown for the rubber. The mill opening was 0.058 inch. The test slabs were cured 24 hours after mixing. These specifications were strictly adhered to for all of the batches.

The average roll temperatures at the start and finish of each batch and the stock temperature at the finish of each batch are given in Table II. The low,

TABLE II

MILL ROLL AND STOCK TEMPERATURES

Smoked sheet batches

	Run A	Run B	Run C
Average roll temperature at start	75° F	158° F	212° F
Average roll temperature at finish	121° F	158° F	220° F
Stock temperature at finish	105° F	160° F	205° F

Deresinated Mexican guayule batches

	Run A	Run B	Run C
Average roll temperature at start	75° F	158° F	212° F
Average roll temperature at finish	95° F	170° F	210° F
Stock temperature at finish	117° F	154° F	192° F

medium, and high temperature runs for each rubber are designated as A, B, and C, respectively. It will be noted that the A runs started at 75° F, the B runs at 158° F, and the C runs at 212° F. The tensile strength-time of cure relation for each batch is given in Figure 1.

The data plotted in Figure 1 show only a slight benefit for the higher milling temperatures; in fact the benefit is almost within experimental error. This is in directional agreement with data of Hauser and Le Beau[2], but these investigators neglected to point out that the tensile properties of *Hevea* rubber are

likewise affected to even a greater extent by milling temperature. They stated, moreover, that the milling temperature has no effect on the rate of cure of guayule rubber; whereas their plotted data indicate that the batch milled at the higher temperature cured slower. The authors found that the guayule

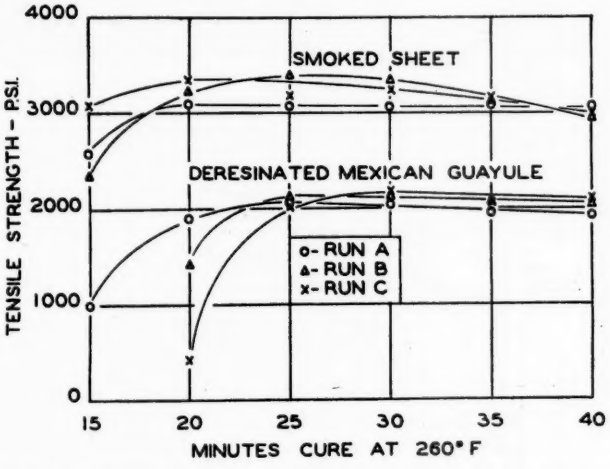

FIG. 1.—Effect of milling temperature on the tensile strength-time of cure relation for loaded smoked-sheet and deresinated Mexican guayule stocks containing benzothiazyl disulfide-zinc dimethyldithiocarbamate acceleration.

batches milled at 158° and 212° F cured considerably slower than the batch milled at 75° F; the former batches did not cure in 15 minutes at 260° F; while the latter batch reached a tensile strength of 1000 lbs. per sq. in. in this time.

EFFECT OF CURING TEMPERATURE

The effect of curing temperature on tensile strength was found by curing the smoked sheet and deresinated guayule stocks, Recipe No. 1 in Table I, for various times at 250°, 270°, and 290° F. The data are plotted in Figure 2.

It is evident that the curing temperature within the range 250–290° F has little influence on tensile strength at optimum cure. There is a drop of about 200 lbs. per sq. in. in the optimum tensile values between the 250° F cure and the 290° F cure in the case of the smoked sheet stock. The deresinated Mexican guayule stock shows practically no change in optimum tensile values between these temperatures.

Hauser and Le Beau[2] found that lower curing temperatures favored higher optimum tensile strength. However, they used unactivated mercaptobenzothiazole acceleration, which would not be expected necessarily to behave the same as benzothiazyl disulfide-zinc dimethyldithiocarbamate acceleration.

EFFECT OF STEARIC ACID

Several years ago when the authors first started working with guayule rubber, they were advised by H. Boucher, then chemist for the American Rubber Producers, Inc., Salinas, California, that guayule rubber requires more stearic acid than *Hevea* rubber for satisfactory vulcanization. Hauser and Le Beau investigated the stearic acid requirement of a pure-gum guayule stock

accelerated with mercaptobenzothiazole and found that an increase from one part to four parts of stearic acid raised the tensile strength at optimum cure about 1000 lbs. per sq. in. At the time of publication of these data the present authors were completing a comprehensive investigation of guayule rubber compounding, in which variations in the proportions of accelerators, zinc oxide, stearic acid, and sulfur were studied. It had been found that, when using benzothiazyl disulfide-zinc dimethyldithiocarbamate acceleration and a

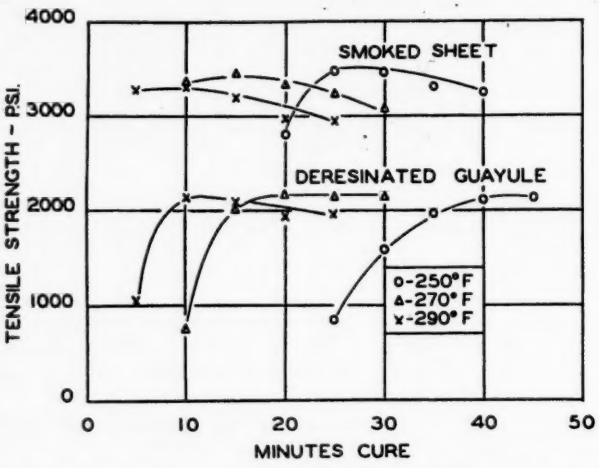

FIG. 2.—Effect of curing temperature on the tensile strength-time of cure relation for loaded smoked-sheet and deresinated Mexican guayule stocks containing benzothiazyl disulfide-zinc dimethyldithiocarbamate acceleration.

Pelletex black loading, stearic acid is not required for optimum tensile strength. It was, therefore, decided to repeat the work of Hauser and Le Beau to find whether the requirement for high stearic acid is peculiar to a pure-gum guayule stock accelerated with mercaptobenzothiazole.

The pure-gum recipe used to determine the effect of stearic acid is No. 2 in Table I. This recipe is similar to the recipe employed by Hauser and Le Beau, except that the sulfur has been reduced from 3 to 2.5 parts. Batches containing the rubbers listed in Table III were prepared. The stearic acid

TABLE III

RUBBERS USED FOR DETERMINING EFFECT OF STEARIC ACID

Rubber	Deresinated by	Content of acetone-soluble substances (percentage)	Content of fibrous substances (percentage)
Smoked sheet		5.1	0.0
Deresinated smoked sheet	Rubber Laboratory	1.6	0.0
Deresinated Mexican guayule	Rubber Laboratory	5.5	0.48
Deresinated domestic guayule, lot No. 1	American Rubber Producers	4.4	0.13
Deresinated domestic guayule, lot No. 2	American Rubber Producers	6.2	0.13
Deresinated domestic guayule, lot No. 3	American Rubber Producers	3.1	0.11
Deresinated domestic guayule, lot No. 4	American Rubber Producers	3.2	0.06

proportions used with each rubber were one part, two and four parts. The tensile strength of the stocks after curing for various times at 270° F are plotted in Figures 3 to 9 inclusive.

It is evident from the plotted data that the tensile strength of all the rubbers is improved by increasing the proportion of stearic acid to four parts. The improvement is about equal for the deresinated guayule rubbers and deresinated smoked sheet. The improvement is somewhat greater for deresinated smoked sheet than for resiniferous smoked sheet. It is clear, nevertheless, that the improvement in tensile strength resulting from increased stearic acid is a characteristic not only of a pure-gum deresinated guayule stock accelerated with mercaptobenzothiazole, but also of a similar smoked sheet stock.

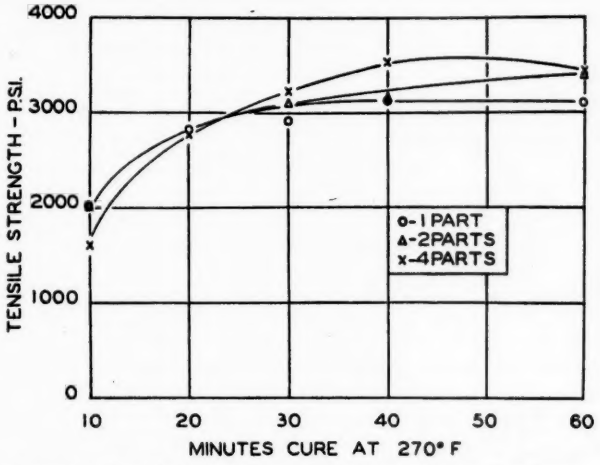

FIG. 3.—Effect of stearic acid on the tensile strength-time of cure relation for a pure-gum smoked-sheet stock containing mercaptobenzothiazole acceleration.

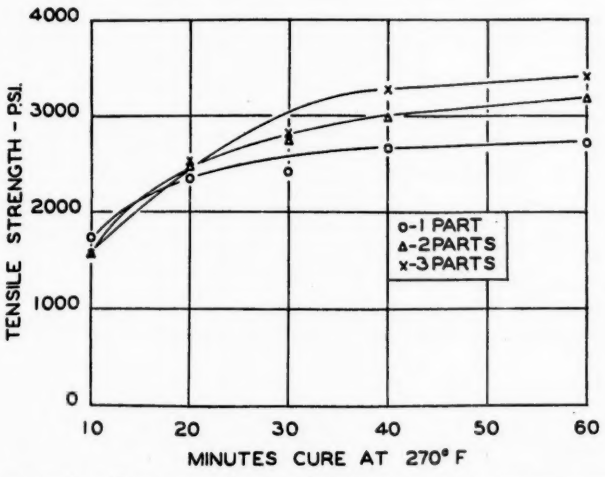

FIG. 4.—Effect of stearic acid on the tensile strength-time of cure relation for a pure-gum deresinated smoked-sheet stock containing mercaptobenzothiazole acceleration.

The fact that a pure-gum *Hevea* stock accelerated with mercaptobenzothiazole reaches its highest tensile strength when four parts of stearic acid are used has been known for some time[3]. The reason that this much stearic acid is not generally used in such a stock is the undesirable bloom of stearic acid

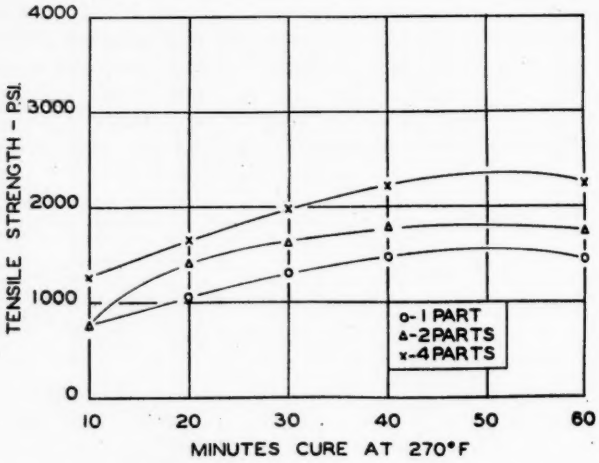

FIG. 5.—Effect of stearic acid on the tensile strength-time of cure relation for a pure-gum deresinated Mexican guayule stock containing mercaptobenzothiazole acceleration.

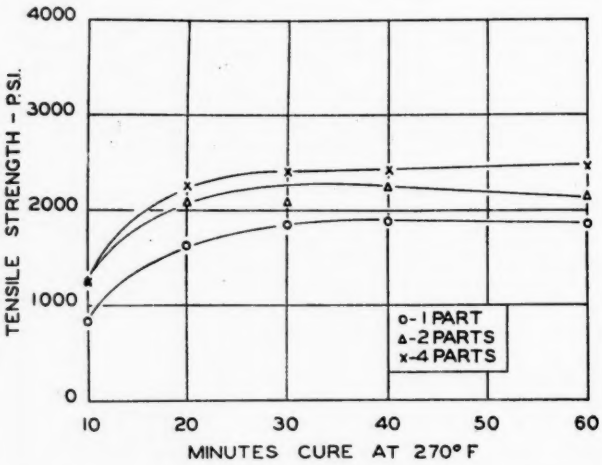

FIG. 6.—Effect of stearic acid on the tensile strength-time of cure relation for a pure-gum domestic deresinated guayule stock containing mercaptobenzothiazole acceleration; lot No. 1.

which may develop before and after cure. The same reason would apply to four parts of stearic acid in a pure-gum deresinated guayule stock.

Previous work[2] has shown that benzothiazyl disulfide activated by zinc methyldithiocarbamate is an outstanding accelerator combination for use in guayule stocks. This accelerator combination produces excellent physical

properties and good resistance to accelerated aging and natural weathering. The authors, therefore, were interested in the effect of stearic acid in guayule stocks containing this accelerator combination. A pure-gum recipe and a recipe containing Pelletex black were employed for this purpose. These

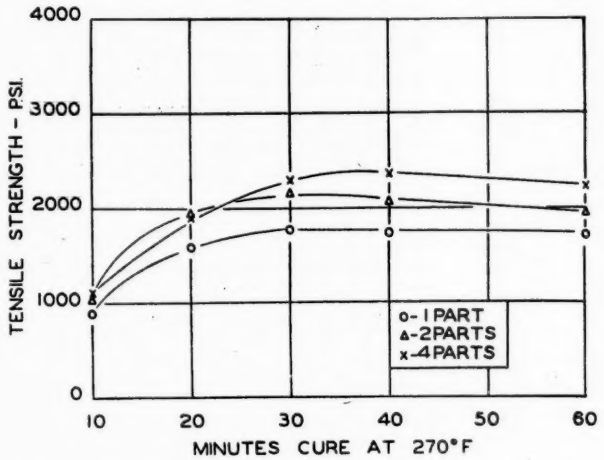

FIG. 7.—Effect of stearic acid on the tensile strength-time of cure relation for a pure-gum domestic deresinated guayule stock containing mercaptobenzothiazole acceleration; lot No. 2.

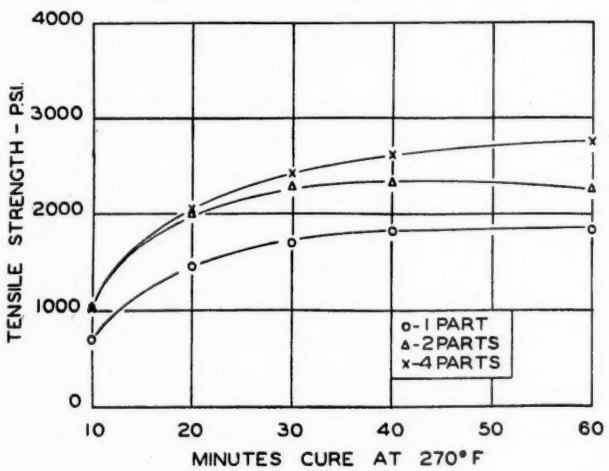

FIG. 8.—Effect of stearic acid on the tensile strength-time of cure relation for a pure-gum domestic deresinated guayule stock containing mercaptobenzothiazole acceleration; lot No. 3.

recipes, Nos. 3 and 4, respectively, in Table I, were tested without stearic acid and with one part, two, three and four parts of stearic acid. The deresinated Mexican guayule rubber used in these recipes is described in Table III. The same recipes were used for compounding smoked-sheet stocks, which were tested for comparison.

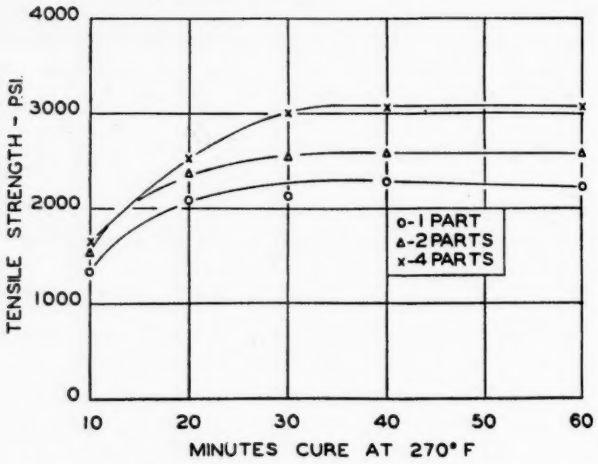

FIG. 9.—Effect of stearic acid on the tensile strength-time of cure relation for a pure-gum domestic deresinated guayule stock containing mercaptobenzothiazole acceleration; lot No. 4.

The curves showing tensile strength *vs.* time of cure at 260° F for the above stocks are shown in Figures 10, 11, 12, and 13. These curves show that the addition of stearic acid to the guayule and smoked-sheet stocks accelerated by benzothiazyl disulfide and zinc dimethyldithiocarbamate does not improve their tensile strength at optimum cure, but does reduce their rates of cure. The reduction in rate of cure is more pronounced with the guayule stock than with the smoked-sheet stock and is more pronounced with the pure-gum stocks than with the loaded stocks.

Further information on the effects of stearic acid in the loaded guayule stock, Recipe No. 4, was obtained by conducting the following tests on the

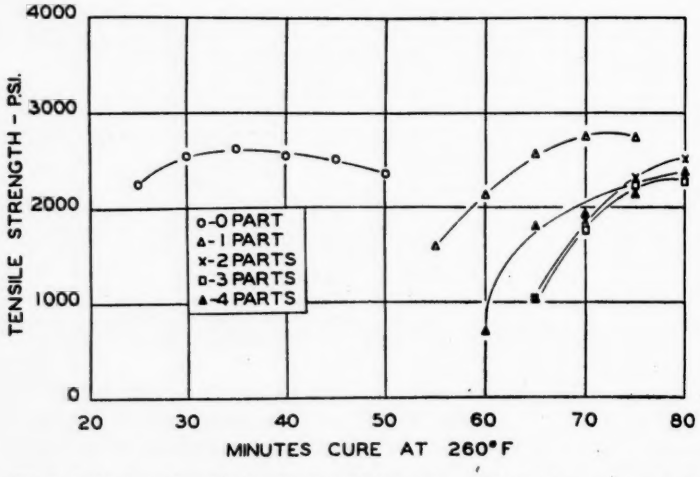

FIG. 10.—Effect of stearic acid on the tensile strength-time of cure relation for a pure-gum deresinated Mexican guayule stock containing benzothiazyl disulfide-zinc dimethyldithiocarbamate acceleration.

optimum cure for each stock: oxygen-bomb aging, tear resistance, Shore hardness, and rebound. The oxygen-bomb aging test consisted of aging A. S. T. M. type C tensile-strength specimens and A. S. T. M. type B tear-resistance speci-

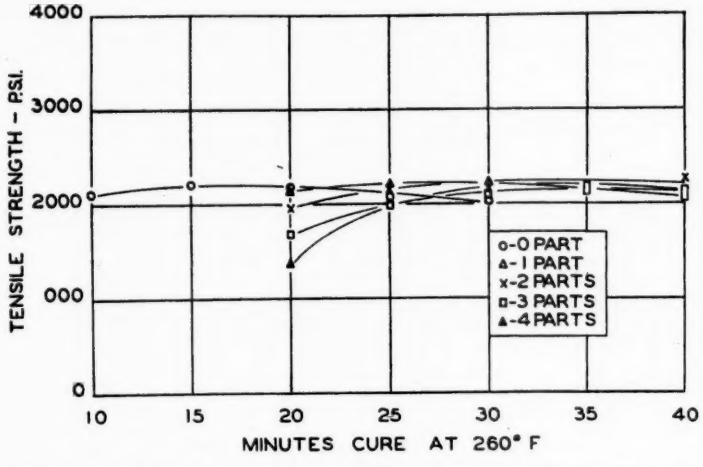

FIG. 11.—Effect of stearic acid on the tensile strength-time of cure relation for a loaded deresinated Mexican guayule stock containing benzothiazyl disulfide-zinc dimethyldithiocarbamate acceleration.

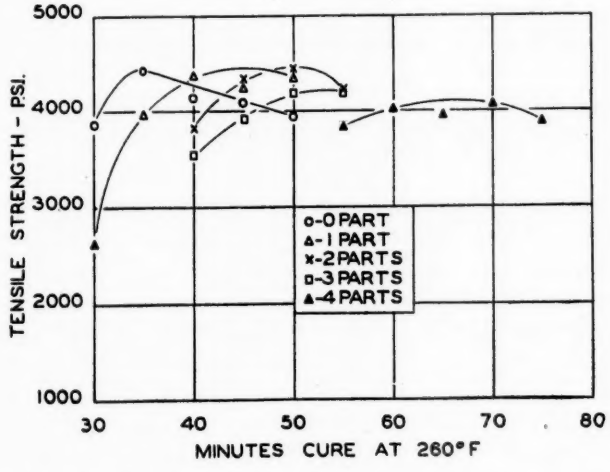

FIG. 12.—Effect of stearic acid on the tensile strength-time of cure relation for a pure-gum smoked-sheet stock containing benzothiazyl disulfide-zinc dimethyldithiocarbamate acceleration.

mens for 24 hours at 158° F under 300 lbs. per sq. in. oxygen pressure. The rebound test was performed with the Goodyear-Healy pendulum, using a 15-degree angle of fall. The initial and aged tensile strengths, ultimate elongation, stress at 300 per cent elongation, initial and aged tear resistance, Shore hardness, and rebound are shown in the form of bar graphs in Figure 14.

Figure 14 shows that increasing the stearic acid content from none to four parts does not improve initial tensile strength, aged tensile strength, ultimate elongation or stress at 300 per cent elongation. The addition of one part stearic acid, however, slightly improves initial tear resistance, aged tear resistance, Shore hardness, and rebound. Increasing the stearic acid above one part brings about no further improvement in any of these properties. It is concluded, therefore, that one part or two parts of stearic acid should be used

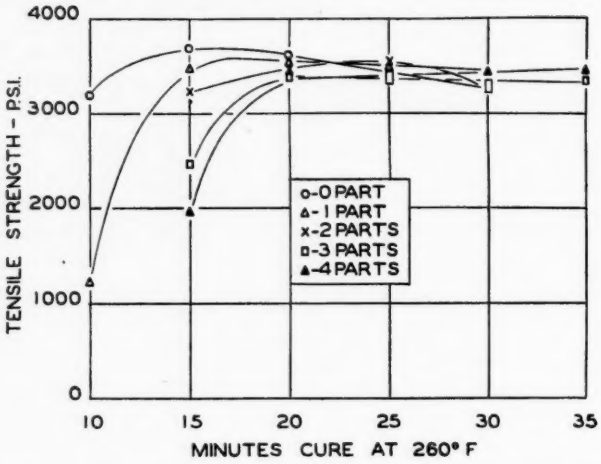

FIG. 13.—Effect of stearic acid on the tensile strength-time of cure relation for a loaded smoked-sheet stock containing benzothiazyl disulfide-zinc dimethyldithiocarbamate acceleration.

in deresinated guayule stocks containing benzothiazyl disulfide-zinc dimethyldithiocarbamate acceleration and Pelletex black loading if the slower rate of cure resulting therefrom is not objectionable.

EFFECT OF OTHER INGREDIENTS INVOLVED IN VULCANIZATION REACTION

It was believed desirable to investigate variations in the amounts of the other compounding ingredients which are involved in the vulcanization reaction: namely, zinc oxide, benzothiazyl disulfide, zinc dimethyldithiocarbamate, and sulfur. This was done in Recipe No. 1, using the deresinated Mexican guayule rubber described in Table III. Only one ingredient was varied at a time. The following variations were tried:

Zinc oxide	2.5-5.0-10.0 parts
Benzothiazyl disulfide	0.8-1.0- 1.2 parts
Zinc dimethyldithiocarbamate	0.1-0.15-0.2-0.25 parts
Sulfur	2.5-2.75-3.0-3.5 parts

The underlined figures are the proportions of the respective ingredients contained in the base recipe.

The various stocks were tested for initial tensile strength, aged tensile strength, ultimate elongation, stress at 300 per cent elongation, initial tear resistance, aged tear resistance, Shore hardness, and rebound. The test re-

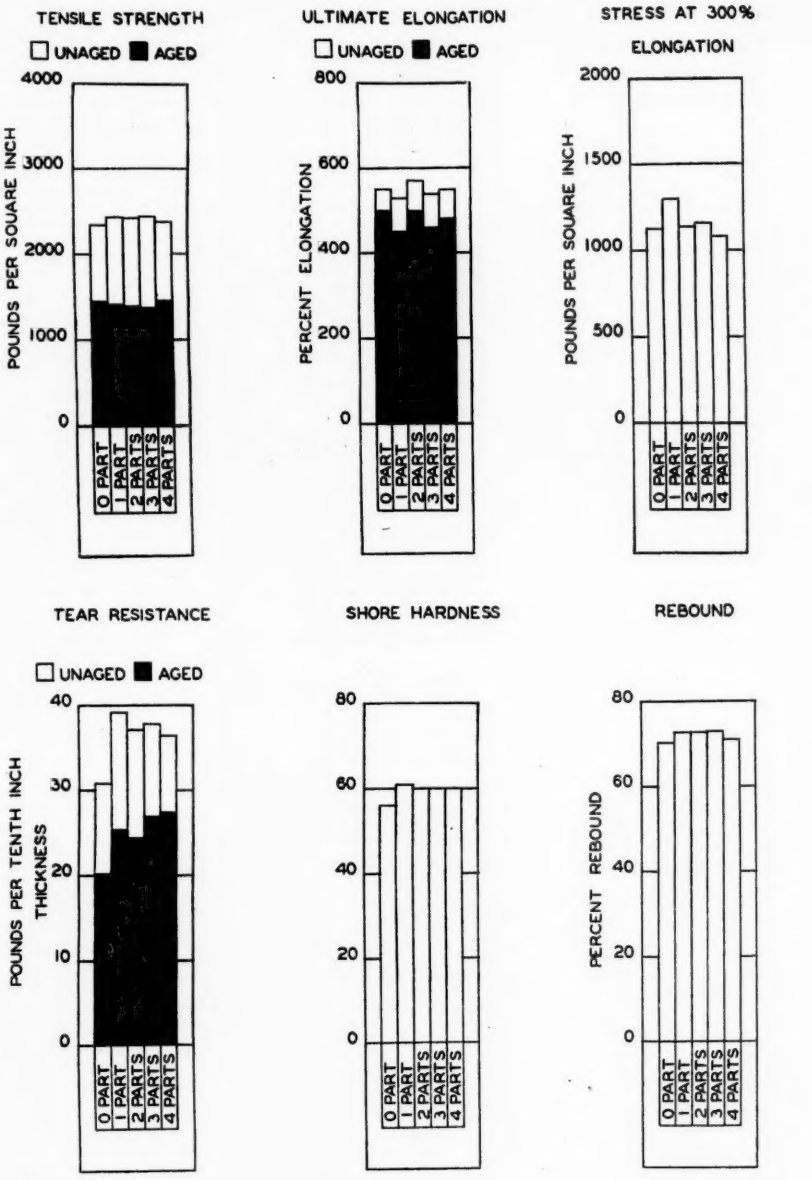

FIG. 14.—Effect of stearic acid on various physical properties. Loaded Mexican deresinated guayule stock; benzothiazyl disulfide-zinc dimethyldithiocarbamate acceleration.

sults showed that none of the variations was an improvement over the base recipe. The differences in properties were so slight in most cases that it is not considered worthwhile to present the data.

QUALITY OF DERESINATED GUAYULE RUBBER

Hauser and Le Beau[3] have stated that, with appropriate compounds, commercially deresinated guayule rubber can result in cured stocks which are equivalent in their physical properties to those prepared from *Hevea* rubber. The authors doubt that this equivalence can be regularly obtained with the deresinated guayule rubbers commercially available. In support of this contention, reference is again made to Figures 3 to 9, inclusive. It is shown in these graphs that stocks prepared from four commercially deresinated guayule rubbers have optimum tensile strengths ranging from 2300 to 3100 lbs. per sq. in.; whereas the smoked-sheet stock has an optimum tensile strength of 3500 lbs. per sq. in. It is evident that the commercially deresinated guayule rubbers now available vary widely in quality, and usually are considerably lower in quality than first-grade *Hevea* rubber.

CONCLUSIONS

The authors conclude, from the work reported herein, that commercially available deresinated guayule rubber may best be compounded in the same manner as *Hevea* rubber, with an expectation of obtaining approximately 75 per cent of the tensile strength of a similar *Hevea* stock. It is concluded further that deresinated guayule rubber may generally be processed and cured in the same manner as *Hevea* rubber without sacrificing quality to a greater extent than is done with *Hevea* rubber.

ACKNOWLEDGMENT

The authors wish to acknowledge the coöperation of Irwin H. Whitthorne and Harold N. Olsen in this investigation.

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[1] See preceding paper in this issue of RUBBER CHEMISTRY AND TECHNOLOGY, and the "Effect of accelerator-curing agent combinations on the resistance to sunlight", by Morris, James and Werkenthin, *India Rubber World* **107**, 31 (1942).
[2] Hauser and Le Beau, *India Rubber World* **106**, 447 (1942); this issue of RUBBER CHEMISTRY AND TECHNOLOGY.
[3] Anon., *Vanderbilt News* **3**, No. 4, 26 (1933).

HEAT RESISTANCE OF NEOPRENE-GN VULCANIZATES *

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Control of heat deterioration is a continuous problem for the chemist. In the case of rubber and synthetic elastomers, the rubber chemist has charted the changes in the physical properties of vulcanized elastomers during heat aging. He has developed many methods for retarding the deterioration of rubber compounds by heat; but with the newer synthetic elastomers the development of methods of retarding deterioration by heat is now an active subject of investigation. The degree of deterioration depends on the methods of compounding and curing the different elastomers, as well as on the conditions of aging. In general, continuous exposure to high temperatures softens natural rubber but hardens synthetic elastomers.

Inherently Neoprene has greater heat resistance than natural rubber[1]. Many investigators have described the heat resistance of rubber vulcanizates, but only a few have reported on the heat resistance of Neoprene vulcanizates, and these reports have been primarily comparisons of given Neoprene vulcanizates with one or more rubber stocks. The compounding of Neoprene (Type GN) for heat resistance was discussed by Catton, Fraser, and Forman[2]. The oxygen bomb aging of Neoprene (Types E and GN) was compared with that of various rubber compositions by Neal, Bimmerman, and Vincent[3].

CRITICAL ANALYSIS OF HEAT AGING

In analyzing the changes in properties of heat-resisting rubber stocks during prolonged exposure to high temperature, a permanent and progressive decline in quality is observed. Tensile strength decreases slightly during the early stages of aging, followed by a rapid drop to ultimate failure. Ultimate elongation usually follows the same trend as tensile strength, while hardness increases slightly, followed by a rapid decrease. During the heat aging of Neoprene, a different pattern is evident: (1) tensile strength drops slightly in the early stages, but the loss seldom exceeds 35 per cent, and thereafter little or no change is observed; (2) ultimate elongation decreases rapidly at first and declines slowly thereafter; and (3) hardness increases rapidly at first and then asymptotically approaches maximum hardness.

Since the tensile strength of practically all Neoprene vulcanizates is not seriously reduced by severe aging conditions, this property is not a satisfactory criterion of age resistance. The magnitude of the changes in elongation and hardness under similar conditions, however, are generally larger; therefore these properties should be carefully studied in evaluating heat-resisting Neoprene vulcanizates. Hardness is considered the more important because ultimate serviceability often depends on it. Furthermore, the development of Neoprene vulcanizates having satisfactory elasticity after heat exposure depends on retarding their hardening during aging. The effects of heat on some

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physical properties must be considered separately because changes in elongation, hardness, and tensile strength cannot always be correlated with changes in resilience, flex resistance, electrical properties, and solvent resistance. However, in this work only changes in elongation and hardness are considered.

Typical aging curves showing the changes in hardness and elongation of normal Neoprene vulcanizates are reproduced in Figures 1 and 2; they are characteristic for all variations of high-temperature exposures. A normal Neoprene compound is defined as one which contains only the necessary curing ingredients, nominal filler loading but not special accelerators, antioxidants, or retarders. Such a compound might have the following formula, and it would usually be cured 30 minutes at 287° F:

Neoprene (Type GN)	100.0
Stearic acid	0.5
Neozone-A (phenyl-α-naphthylamine)	2.0
Extra-light calcined magnesia	4.0
Filler and softener	As desired
Zinc oxide	5.0

As previously stated, hardness rapidly increases during the initial period of aging and then slowly increases as aging progresses. This is illustrated by Figure 1. The difference between starting point A and ending point B is the increase in hardness during aging, and any reduction in this difference constitutes an improvement in heat resistance. Compounding changes in filler and softener content control the position of the curve on the scale, but do not affect the magnitude of the increase in hardness except when the stock is heavily loaded and the vulcanizate approaches its maximum hardness.

Since extended curing is known to increase hardness, it is a reasonable assumption that the initial aging period represents a prolongation of cure. It follows that the prolongation of cure to produce a stock having a higher original hardness should result in a vulcanizate which undergoes less change during heat aging. Hence, on heat aging, curve AB for the normal cure would assume the slope $A'B'$, which is somewhat comparable to the EB portion of the original AB curve. As the increase from A' to B' is less than from A to B, a high state of cure in Neoprene (Type GN) vulcanizates should result in better heat resistance. Furthermore, a longer time is required to show a given percentage increase in hardness on curve $A'B'$ than on curve AB, and this means a slower rate of aging.

Figure 2 illustrates that the rate of change in extensibility is similar to the rate of change in hardness. There is a large decrease in extensibility during heat aging of a normally cured vulcanizate. The curve would be shifted from CD to $C'D'$ by increasing the state of cure of the vulcanizate. Since C' to D' is a smaller change than C to D and the $C'D'$ curve approximates the FD portion of CD, changes in elongation during heat exposure, like those of hardness, should be reduced by an extension of cure.

The fact that a long cure results in a stiffer stock does not prevent the use of this method for improving heat resistance. If the elongation and hardness are outside of a specified or desired range, the filler and softener content can be adjusted to obtain the desired original properties. For example, if the desired hardness is A in Figure 1, a reduction in filler, increase in softener, or both, would meet the requirements with a high state of cure. Curve $A'B'$ would shift to AB'' on the scale, and the increase in hardness from A to B'' would be the same as from A' to B'. This would result in a general increase in elongation, as shown by curve C'' to D'' in Figure 2.

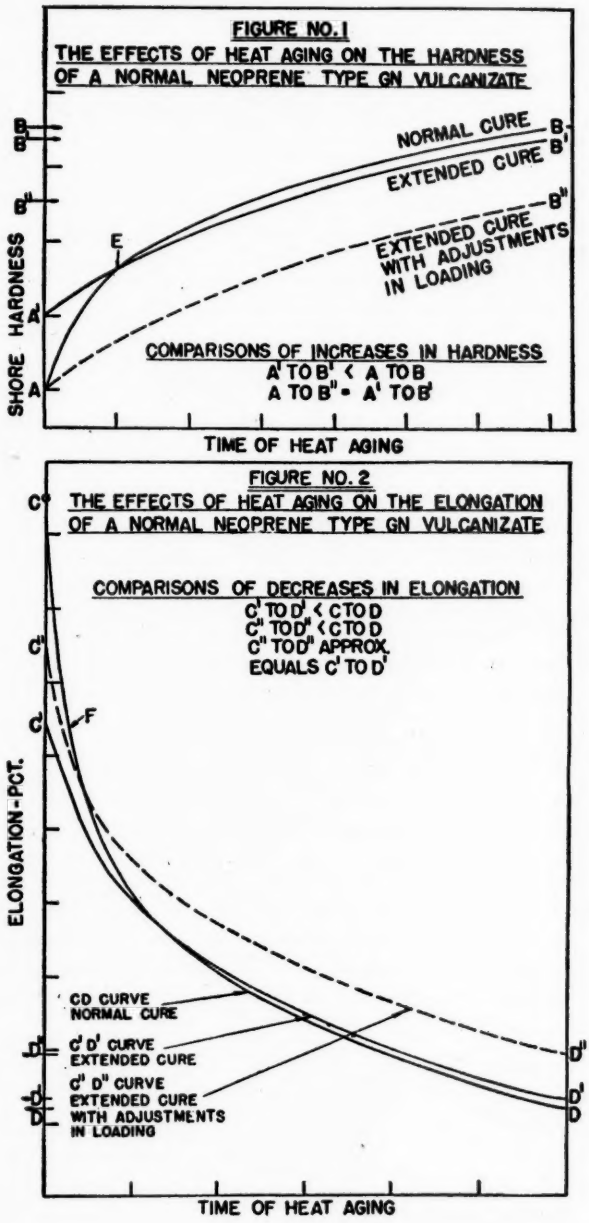


FIGURE NO. 1
THE EFFECTS OF HEAT AGING ON THE HARDNESS OF A NORMAL NEOPRENE TYPE GN VULCANIZATE
NORMAL CURE
EXTENDED CURE
EXTENDED CURE WITH ADJUSTMENTS IN LOADING
SHORE HARDNESS
COMPARISONS OF INCREASES IN HARDNESS
A' TO B' < A TO B
A TO B" = A' TO B'
TIME OF HEAT AGING
FIGURE NO. 2
THE EFFECTS OF HEAT AGING ON THE ELONGATION OF A NORMAL NEOPRENE TYPE GN VULCANIZATE
COMPARISONS OF DECREASES IN ELONGATION
C' TO D' < C TO D
C" TO D" < C TO D
C" TO D" APPROX. EQUALS C' TO D'
ELONGATION - PCT.
CD CURVE NORMAL CURE
C' D' CURVE EXTENDED CURE
C" D" CURVE EXTENDED CURE WITH ADJUSTMENTS IN LOADING
TIME OF HEAT AGING

The effects of accelerators or retarders cannot be overlooked. Accelerators, by increasing the rate of cure, would be expected to affect the heat resistance in a manner similar to that of extending the cure. The use of accelerators has the added advantage of shortening the time of vulcanization.

Retarders, by decreasing the rate of cure, would be expected to impair the heat resistance.

APPLICATION

In applying a test situation to the hypothesis just outlined, Neoprene (Type GN) was compounded in a heat-resisting formula. Thirty-two parts of semireinforcing carbon black were added, and the resulting stock was used as the control (1336N–47). The normal cure of this stock is 30 minutes at 287° F, and the original hardness obtained was 57. Reducing the carbon black to 20.0 parts produced a stock (1336N–46) having an original hardness of 52 with a normal cure. Increasing the carbon black to 43.0 parts (1336N–48) produced a stock having an original hardness of 63. The stock containing 20 parts of carbon black was brought to an original hardness of 57 by two methods: (1) by extending the cure to 90 minutes at 324° F (1336N–46), and (2) by the use of an accelerator, Permalux (di-*o*-tolylguanidine salt of dicatechol borate, 1336N–49). The original hardness of the stock containing 43.0 parts of carbon black was reduced to 59 by adding a retarder, benzothiazyl disulfide (1336N–50).

Standard test methods were used[4] with aging periods up to 24 days in the 121° C air oven and up to 6 days in the 150° C air oven. The physical properties of these compounds and the data obtained after aging are summarized in Table I.

These data provide the answer to the following questions arising from the hypothesis. For a given hardness, does a stock with less filler having a high state of cure have better heat resistance? Does the addition of accelerator have the same effect as an extended cure? Does a compound having greater loading and added retarder for obtaining hardness have better heat resistance because the Neoprene content would be less? Does heat resistance improve as loading by filler increases? In discussing these questions, all references are made to curves showing the changes in elongation and hardness during aging in the 121° C air oven. The results obtained in the 150° C oven were similar except that the changes occurred in a much shorter time.

The curves in Figures 3 and 4 show that the simultaneous use of lower filler and longer cure to produce a given hardness results in greater heat resistance than the use of normal filler loading and normal cure. The original hardness of the two vulcanizates was 57. During aging in the 121° C air oven, the highly cured vulcanizate increased 27 points in hardness, compared with 32

TABLE I

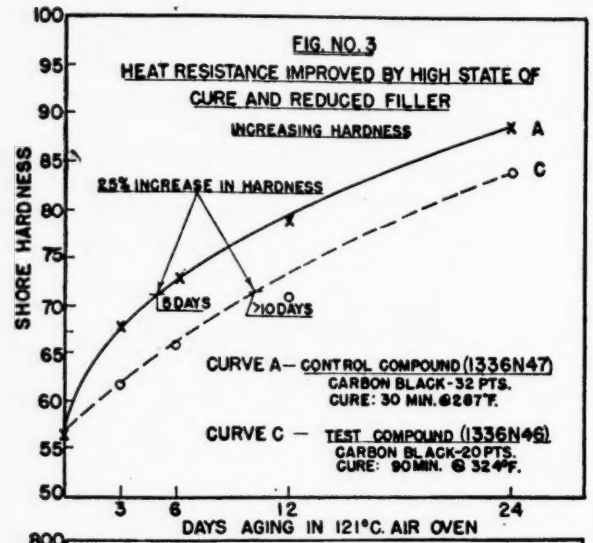
EFFECTS OF STATE OF CURE, QUANTITY OF FILLER, CHEMICAL ACCELERATOR, AND CHEMICAL RETARDER ON HEAT RESISTANCE

Compound No. 1336N–	46	47	48	49	50
Neoprene (Type GN)	100.0	100.0	100.0	100.0	100.0
Stearic acid	0.5	0.5	0.5	0.5	0.5
Neozone-A	2.0	2.0	2.0	2.0	2.0
MUF[a]	1.0	1.0	1.0	1.0	1.0
Extra-light calcined magnesia	4.0	4.0	4.0	4.0	4.0
Semireinforcing carbon black	20.0	32.0	43.0	20.0	43.0
Zinc oxide	10.0	10.0	10.0	10.0	10.0
Permalux	...	...	...	1.0	...
Benzothiazyl disulfide	...	...	...	...	1.5

[a] The antioxidant *N*-*p*-tolyl-*N*[1]-*p*-tolylsulfonyl-*p*-phenylenediamine.

TABLE I—(*Continued*)

Compound and cure	Aging Days	Aging Temp. (° C)	Stress (lbs. per sq. in.) 100%	300%	500%	Tensile strength (lbs. per sq. in.)	Elongation at break (%)	Shore hardness
1336N–46, 30 min. at 287° F	Original		175	675	1350	3075	950	52
	3	121	350	1475	...	2200	455	62
	6	121	550	1875	...	2200	350	67
	12	121	850	...	...	2075	235	74
	24	121	2150	...	...	2325	115	85
	0.75	150	575	...	...	1550	245	64
	1.5	150	950	...	...	1475	160	70
	3	150	...	...	...	1225	60	81
	6	Too brittle to test						
1336N–46, 90 min. at 324° F	Original		250	1050	2050	2800	645	57
	3	121	350	1475	...	2250	430	62
	6	121	500	1900	...	2250	350	66
	12	121	825	...	...	2050	230	71
	24	121	1825	...	...	2550	145	84
	0.75	150	475	...	...	1600	280	64
	1.5	150	800	...	...	1375	150	69
	3	150	...	...	...	1175	60	79
	6	Too brittle to test						
1336N–47, 30 min. at 287° F	Original		300	1125	1850	2625	780	57
	3	121	650	2050	...	2350	370	68
	6	121	800	...	...	2350	270	73
	12	121	1400	...	...	2450	205	79
	24	121	...	...	...	2400	90	89
	0.75	150	725	...	...	1825	210	69
	1.5	150	1425	...	...	1650	120	75
	3	150	...	...	...	1475	50	85
	6	Too brittle to test						
1336N–48, 30 min. at 287° F	Original		400	1500	2125	2250	620	63
	3	121	825	2450	...	2475	315	74
	6	121	1175	...	...	2450	215	79
	12	121	1825	...	...	2400	130	83
	24	121	...	...	...	2800	80	94
	0.75	150	1125	...	...	1800	160	75
	1.5	150	1600	...	...	1600	100	81
	3	150	...	...	...	1200	20	90
	6	Too brittle to test						
1336N–49, 30 min. at 287° F	Original		350	1150	2150	2625	605	58
	3	121	475	1900	...	2175	335	66
	6	121	650	...	...	2100	250	70
	12	121	1150	...	...	2100	185	77
	24	121	...	...	...	2775	95	88
	0.75	150	700	...	...	1650	220	69
	1.5	150	...	...	...	1200	95	74
	3	150	...	...	...	1100	30	85
	6	Too brittle to test						
1336N–50, 30 min. at 287° F	Original		275	1250	1925	2200	730	59
	3	121	850	2275	...	2400	355	72
	6	121	1075	...	...	2550	265	77
	12	121	1650	...	...	2575	180	81
	24	121	...	...	...	3000	90	91
	0.75	150	900	...	...	1975	200	73
	1.5	150	1650	...	...	1650	100	79
	3	150	...	...	...	1350	35	88
	6	Too brittle to test						



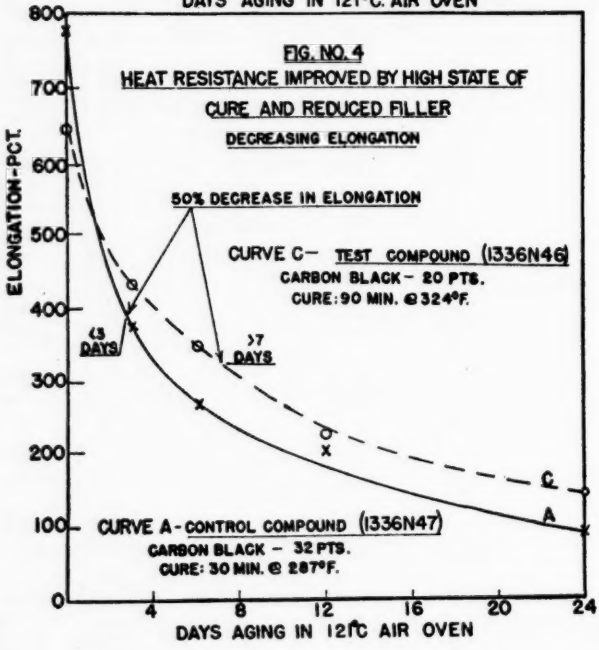
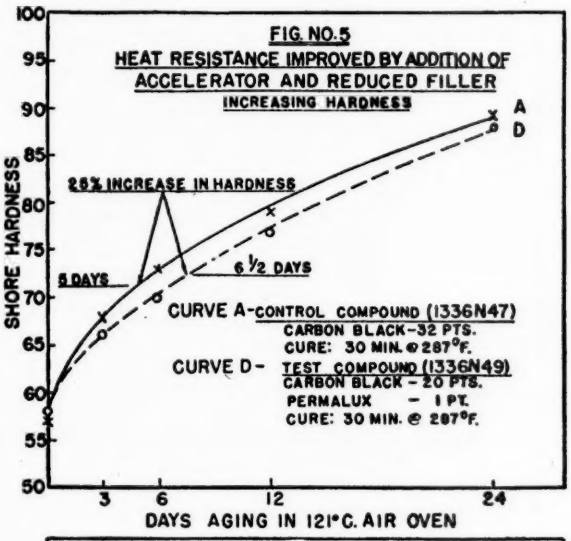


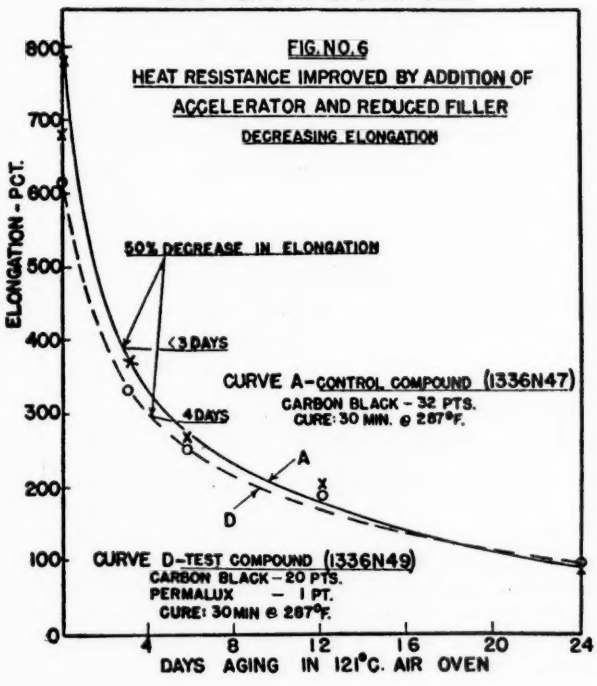
FIG. NO. 4
HEAT RESISTANCE IMPROVED BY HIGH STATE OF CURE AND REDUCED FILLER
DECREASING ELONGATION
50% DECREASE IN ELONGATION
CURVE C— TEST COMPOUND (1336N46)
CARBON BLACK - 20 PTS.
CURE: 90 MIN. @ 324°F.
<3 DAYS
>7 DAYS
C
A
CURVE A - CONTROL COMPOUND (1336N47)
CARBON BLACK - 32 PTS.
CURE: 30 MIN. @ 287°F.
ELONGATION-PCT.
DAYS AGING IN 121°C AIR OVEN

points for the control stock. In addition, an analysis of the curve for compound 1336N–46 in Figure 3 shows that the rate of aging is lower for the highly cured vulcanizate because it must age a longer time to reach a given percentage increase in hardness. As expected, Figure 4 illustrates that the same composition changes least in elongation during aging. About 7 days was required for the highly cured stock to lose 50 per cent of its elongation, compared with less than 3 days for the control vulcanizate. It is interesting to note that the

elongation of the highly cured compound is greater than the base stock after aging begins. This is desirable, and it will be shown later that this is a function of loading rather than one of state of cure.

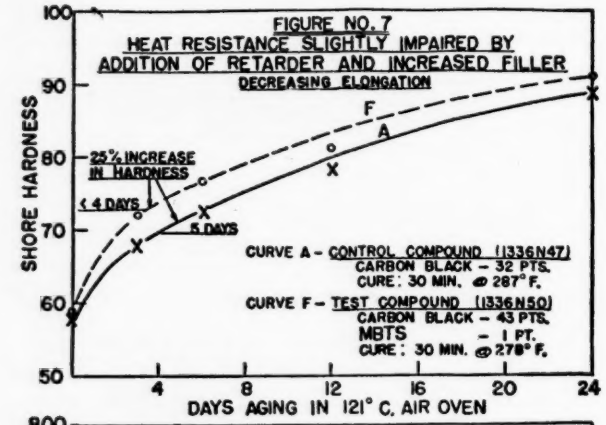
Figures 5 and 6 show that an accelerator (compound 1336N–49) can be used to approximate the effects of prolonged cure. However, the efficiency of

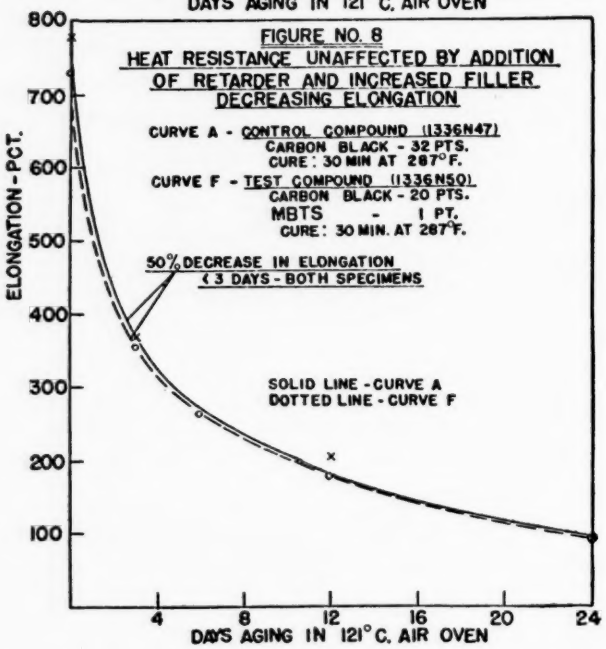




this method is somewhat inferior to that of obtaining a high state of cure by increasing the time or temperature.

The addition of a retarder (compound 1336N–50), such as benzothiazyl disulfide, to a stock containing additional filler slightly reduces rather than





improves heat resistance (Figures 7 and 8). The conclusion regarding retarders must be qualified. Benzothiazyl disulfide reduces the state of cure throughout the range; therefore, if it is present, the time required to obtain a high state of cure for heat resistance would be greatly increased. On the other hand, a material such as sodium acetate[5], that retards at low-temperature cures only, will not affect the heat resistance.

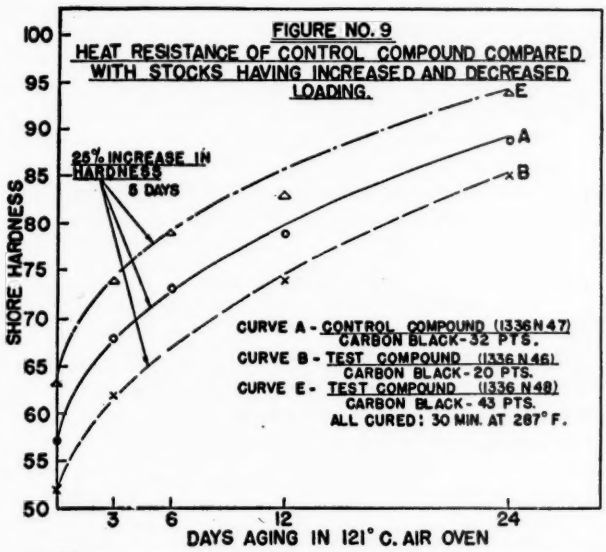


FIGURE NO. 9
HEAT RESISTANCE OF CONTROL COMPOUND COMPARED WITH STOCKS HAVING INCREASED AND DECREASED LOADING.
25% INCREASE IN HARDNESS
5 DAYS
SHORE HARDNESS
DAYS AGING IN 121° C. AIR OVEN
CURVE A - CONTROL COMPOUND (1336N47) CARBON BLACK-32 PTS.
CURVE B - TEST COMPOUND (1336N46) CARBON BLACK-20 PTS.
CURVE E - TEST COMPOUND (1336N48) CARBON BLACK-43 PTS.
ALL CURED: 30 MIN. AT 287° F.

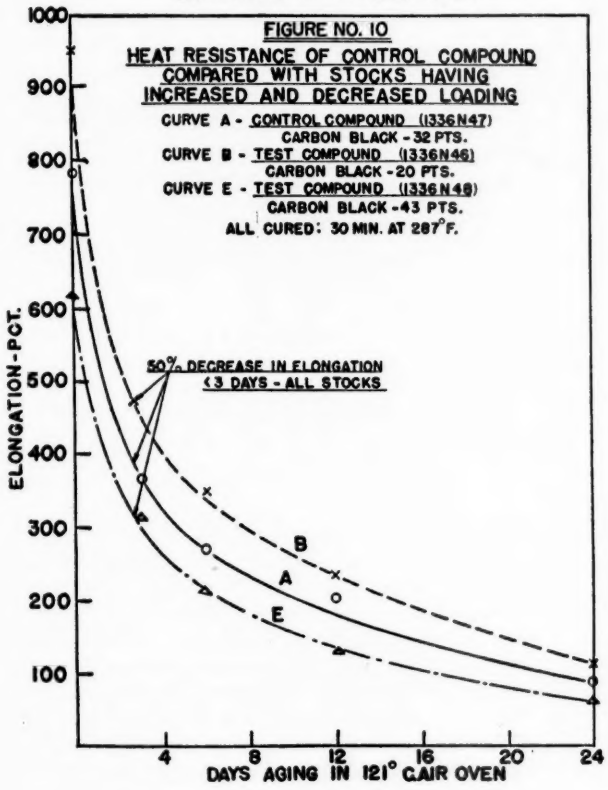


FIGURE NO. 10
HEAT RESISTANCE OF CONTROL COMPOUND COMPARED WITH STOCKS HAVING INCREASED AND DECREASED LOADING
CURVE A - CONTROL COMPOUND (1336N47) CARBON BLACK-32 PTS.
CURVE B - TEST COMPOUND (1336N46) CARBON BLACK-20 PTS.
CURVE E - TEST COMPOUND (1336N48) CARBON BLACK-43 PTS.
ALL CURED: 30 MIN. AT 287°F.
50% DECREASE IN ELONGATION (3 DAYS - ALL STOCKS
ELONGATION-PCT.
DAYS AGING IN 121° C AIR OVEN

Changes in filler loading have a significant effect on the absolute value of ultimate elongation or hardness, both before and after aging, but do not alter the magnitude of the changes that take place during heat exposure, *i.e.*, the heat resistance. As shown by Figures 9 and 10, the rate of aging as based on a 25 per cent increase in hardness or a 50 per cent decrease in elongation is the same for the stocks containing 20.0, 32.0, and 43.0 parts of semireinforcing carbon black.

The changes in elongation and hardness illustrated in Figures 3 to 10 show that a high state of cure would be essential for obtaining the maximum heat

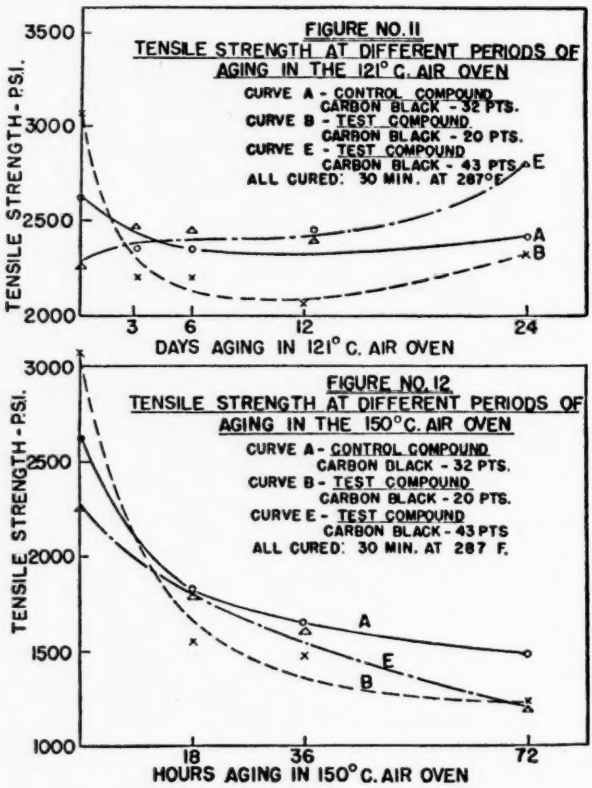


FIGURE NO. 11
TENSILE STRENGTH AT DIFFERENT PERIODS OF AGING IN THE 121° C. AIR OVEN
CURVE A - CONTROL COMPOUND CARBON BLACK - 32 PTS.
CURVE B - TEST COMPOUND CARBON BLACK - 20 PTS.
CURVE E - TEST COMPOUND CARBON BLACK - 43 PTS.
ALL CURED: 30 MIN. AT 287°F
TENSILE STRENGTH - P.S.I.
3500
3000
2500
2000
3
6
12
24
DAYS AGING IN 121° C. AIR OVEN
FIGURE NO. 12
TENSILE STRENGTH AT DIFFERENT PERIODS OF AGING IN THE 150° C. AIR OVEN
CURVE A - CONTROL COMPOUND CARBON BLACK - 32 PTS.
CURVE B - TEST COMPOUND CARBON BLACK - 20 PTS.
CURVE E - TEST COMPOUND CARBON BLACK - 43 PTS
ALL CURED: 30 MIN. AT 287 F.
TENSILE STRENGTH - P.S.I.
3000
2500
2000
1500
1000
18
36
72
HOURS AGING IN 150° C. AIR OVEN

resistance in most applications. Since a 90-minute cure at 324° F may be difficult to obtain, a suggested minimum cure for heat-resisting Neoprene (Type GN) stocks is 40 minutes at 307° F (60 pounds per square inch steam pressure). With the minimum cure, a higher state of cure would be obtained by using a combination of accelerator, Permalux, and a selective retarder, sodium acetate. It is obvious that the absolute values of hardness depend on the thickness of the slab. Tests on specimens 0.250 inch instead of 0.090 inch thick show the same general effects but give absolute hardness values ranging from 2 to 7 points lower. The data in Table I show that when aging is carried out at 150° instead of 121° C, the same relations exist between the compounds. At the higher temperature, changes in elongation are obtained

approximately eight times faster and changes in hardness are obtained approximately five times faster.

TENSILE STRENGTH

As previously stated, tensile strength deterioration is not considered a good criterion for evaluating heat resistance. This is illustrated by comparing the tensile strength curves in Figures 11 and 12 with the elongation and hardness curves in Figures 3 to 10, inclusive. The absolute tensile strength values are above a serviceable minimum, but the specimens have hardened to a point where they are no longer serviceable.

COMPOUNDING AND PRACTICAL APPLICATION

The previously described base formula for heat-resisting Neoprene (Type GN) vulcanizates contains all ingredients necessary for heat or natural aging. Antioxidant and zinc oxide are essential. The former is not added to Neoprene (Type GN) during manufacture, and must be included in all compositions. Zinc oxide is required for good natural aging and significantly improves heat aging. Magnesia is included to balance the physical properties of the vulcanizate, and stearic acid is included for processing. The general use of these materials was discussed previously[2].

The data in Table II show that the base formula (1336N–62) used to study the effect of state of cure is not the only Neoprene (Type GN) composition

TABLE II

HEAT RESISTANCE OF NEOPRENE TYPE GN COMPOUNDS

Compound 1336N–	58	59	60	61	62	63	64
Neoprene (Type GN)	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Stearic acid	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Neozone-A	2.0	...	2.0	2.0	2.0	2.0	2.0
MUF	...	...	...	...	1.0	1.0	...
Extra-light calcined magnesia	...	4.0	...	4.0	4.0	4.0	...
Semireinforcing carbon black	28.8	28.8	28.8	28.8	28.8	28.8	28.8
FF wood rosin	...	...	...	...	...	10.0	...
Zinc oxide	...	10.0	10.0	10.0	10.0	10.0	10.0
Litharge	...	...	...	...	...	...	20.0
STRESS-STRAIN RESULTS (ALL STOCKS CURED 30 MINUTES AT 287° F)							
Original							
Stress at 300% (lbs. per sq. in.)	800	1225	600	1100	1075	1000	1025
Tensile strength (lbs. per sq. in.)	2575	2650	2875	2825	2700	2775	2700
Elongation at break (%)	695	675	900	740	720	800	695
Shore hardness	52	59	53	59	60	59	58
After 7-day exposure in 121° C oven							
Tensile strength (lbs. per sq. in.)	375	1650	1725	2050	2150	2100	1300
Elongation at break (%)	40	110	225	200	280	370	155
Shore hardness	75	79	72	77	77	75	71
Retained tensile strength (%)	14.6	62.3	60.0	72.6	79.6	75.9	48.2
Retained elongation (%)	5.8	16.3	25.0	27.1	38.9	46.2	22.3
After 21 days in oxygen bomb (70° C at 300 lbs. per sq. in.)							
Stress at 300% (lbs. per sq. in.)	...	...	1050	1500	1525	1600	1300
Tensile strength (lbs. per sq. in.)	Failed	1525	2375	2050	1925	1875	2150
Elongation at break (%)	in	200	760	520	520	485	620
Shore hardness	14	81	61	68	70	72	65
Retained tensile strength (%)	days	57.5	82.6	72.6	71.4	67.6	79.3
Retained elongation (%)	...	29.7	84.5	70.3	72.2	60.6	90.8

that has good heat resistance or has extremely long life during natural aging. However, extensive laboratory tests and practical experience have shown that this combination is preferred because of general excellent physical properties after vulcanization. The data on compounds 1336N–58 and 59 show the necessity of including antioxidant and metallic oxide. Compounds 1336N–60, 61, and 64 illustrate the effects of the metallic oxides:

1. Magnesia stiffens vulcanizates before and after aging but imparts a greater retention of tensile strength after heat aging.

2. Zinc oxide improves the elasticity and thereby helps to limit stiffening before or after aging.

3. Lead oxide greatly limits hardening during heat exposure, but vulcanizates containing it do not retain tensile strength or extensibility as well as others.

A comparison of compounds 1336N–61 and 62 shows the improved extensibility after aging caused by the addition of MUF. This effect is even more pronounced than the figures indicate. Finally, from the standpoint of heat resistance exclusively, the base stock plus FF wood rosin (compound 1336N–63) gives the best heat service. Greater extensibility before and after aging is obtained by the use of rosin. The general use of FF wood rosin is slightly limited because it tends to activate low-temperature curves and increases heat generation during flexing.

Inert fillers and softeners must be used for loading practical stocks. The softeners must be carefully selected on a basis of heat stability and volatility.

TABLE III

USUAL CHANGES IN PROPERTIES DURING HEAT SERVICE

Property	Effect
Stress at given elongation	Increases
Tensile strength	Depends on filler content and method of compounding
Elongation	Decreases
Hardness	Increases
Resilience	Decreases
Percentage compression-set, methods A and B	Increases when aged during compression but decreases when aged before compression
Water absorption	Increases
Oil absorption	Decreases
Freeze resistance	Usually decreases

The over-all physical properties of the unaged vulcanizates must be considered and the action of heat on them is a factor.

Table III summarizes the changes usually observed in many of the physical and chemical properties of Neoprene (Type GN) vulcanizates during aging. As previously indicated, some properties can be correlated with changes in stress-strain properties.

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EFFECT OF PETROLEUM PRODUCTS ON NEOPRENE VULCANIZATES

EFFECT OF GASOLINES *

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E. I. DU PONT DE NEMOURS & COMPANY, INC., WILMINGTON, DELAWARE [1]

The third paper of this series[2] showed that the Diesel index may be used as a criterion of the swelling effect of kerosenes and kerosene-benzene blends on Neoprene. It was erroneously stated, however, that "swelling caused by kerosene is not a simple function of the . . . aniline point". A recheck of the data, together with additional work, indicates that the aniline point may be used as a criterion of the swelling power of kerosenes, but this correlation is not so precise as with the Diesel index. This is particularly true in the case of kerosene-benzene blends when benzene predominates in the blend. As with kerosenes, the aniline point or Diesel index may be used as an indication of the swelling power of gasolines, and thus these constants may be used to specify standard immersion media of these types.

TABLE I

SUMMARY OF DATA FOR GASOLINES

Sample number	Description	A. P. I. gravity (60° F)	Aniline point (° F)	Diesel index	Refractive index	Maximum volume increase of Neoprene at 27.8° C
1	Commercial motor fuel	60.6	115.5	69.99	1.4340	54.0
2	Commercial motor fuel	62.4	110.5	68.95	1.4380	56.5
3	Commercial motor fuel	61.8	111.0	68.60	1.4375	56.5
4	Commercial motor fuel (unleaded)	59.7	103.0	61.49	1.4450	63.4
5	Commercial motor fuel (unleaded)	59.7	114.5	68.36	1.4165	52.9
6	No. 5 + 1 cc. $Pb(C_2H_5)_4$ per gal.	59.1	114.5	67.67	1.4160	54.5
7	No. 5 + 2 cc. $Pb(C_2H_5)_4$ per gal.	58.6	114.5	67.10	1.4175	54.3
8	No. 5 + 3 cc. $Pb(C_2H_5)_4$ per gal.	58.1	114.5	66.52	1.4151	53.1
9	Straight-run stock	67.7	133.5	90.38	1.4098	41.2
10	50 : 50 No. 9 : No. 13	61.6	116.5	71.76	1.4276	52.0
11	40 : 60 No. 9 : No. 13	60.3	113.0	68.15	1.4267	55.0
12	30 : 70 No. 9 : No. 13	59.3	109.0	64.64	1.4282	57.3
13	Cracked stock	56.3	99.5	56.02	1.4372	65.0
14	No. 13 + antioxidant	56.0	98.0	54.88	1.4359	69.6
15	Isoöctane	71.7	176.0	126.19	1.3904	18.5

The Neoprene composition used in the work was identical with that used in the previous investigations[3]. The specimens were prepared for the volume-increase test as previously described. The physical data for, and the description of, the gasolines used in the swelling tests are shown in Table I. Also

* Reprinted from *Industrial and Engineering Chemistry*, Vol. 35, No. 9, pages 947–948, September 1943. This paper was presented before the Division of Rubber Chemistry at the 105th Meeting of the American Chemical Society, Detroit, Michigan, April 15–16, 1943.

shown is the volume increase after immersion of the Neoprene specimens in the gasolines at 27.8° C (82° F). The results shown are those of the maximum swelling. The immersions were continued for 14 days, but maximum swelling values were attained, except in the case of isoöctane, within 3 days. The volume increases at the end of 14 days were the same, within the experimental error, as the results shown in Table I. Because of the volatility of gasoline, care was taken to make the necessary weighings as soon as possible after removal of the specimens from the gasoline.

In Figure 1, the logarithm of maximum swelling plotted against Diesel index gives a straight-line relation. The plot for isoöctane (Sample 15) is the

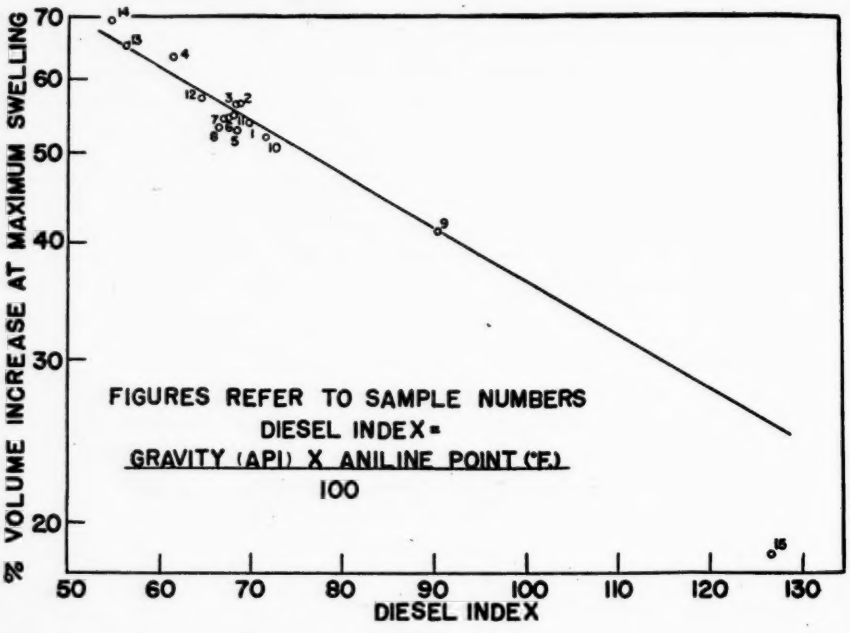

FIG. 1.

swelling after 14-days' immersion, and does not fall on the curve. This material has very little swelling power, and consequently the time necessary to reach maximum or equilibrium swelling is probably considerably in excess of 14 days. If the aniline point is substituted for the Diesel index, a good correlation is also obtained; but it is felt that the latter is a more precise criterion. For instance, in the case of Samples 5, 6, 7, and 8 (showing the effect of the addition of tetraethyl lead), no change was observed in the aniline point, but the Diesel index and swelling results showed that the addition of tetraethyl lead did affect these properties.

Practically all commercial motor fuels (gasolines) represent blends of straight-run and cracked stocks. However, the Diesel index may be used as a criterion of swelling of either type of stock or of intermediate blends as indicated by Samples 9, 10, 11, 12, and 13. As would be expected, a straight-run stock has considerably less swelling effect than a cracked stock. Sample 14 was prepared by adding 0.0043 per cent of a commercial antioxidant (du Pont

gasoline antioxidant, Solution 14) to cracked stock Sample 13. The swelling results indicate that some commercial antioxidants, at least, increase the swelling power of gasolines containing them.

Comparison of the swelling results in Table I with those in Table I of the preceding paper[2] shows that commercial gasolines do not vary in swelling power so much as commercial kerosenes, and that the average swelling effect of the gasolines is a little greater.

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VULCANIZATION OR OTHER HEAT TREATMENT BY ELECTRICAL CONDUCTION *

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This communication relates to the heating of plastic materials of a semiconducting nature by passing electricity through them. In particular, it relates to the vulcanization of rubber and rubberlike materials, including Neoprene, with heat generated by the conduction of an electric current and, similarly, it relates to the heat treatment of thermosetting plastics by conduction of an electric current.

It is well known that all electrical conductors are heated to some extent by the passage of an electric current. This heating is a direct consequence of internal resistance. The effect so obtained is proportional to the electrical energy absorbed, and is expressed by the equation: power = I^2R, in which I. is the current in amperes between two points and R is the corresponding resistance in ohms. The unit of power is the watt.

Others have used electrical means of heating unvulcanized rubber, but the disclosures differ fundamentally from this proposal. For example, Neerlye[1] coils a steel ribbon and an uncured rubber belt in a spiral and heats the coil by passing electricity through the steel. Newton[2] claims vulcanization by a beam of electrons from a cathode ray tube. The most significant disclosure is by Dufour.[3] This claims the "process for the vulcanization of rubber characterized by the feature that the rubber to be heat-treated is arranged as a dielectric between the electrodes of an electric condenser to which there is applied a high frequency alternating current of a periodicity of several million cycles per second". This patent is characterized by utilization of high-frequency fields of the order of several megacycles per second. Further, it is not required in induction curing with high-frequency current that the electrodes be in actual mechanical contact with the rubber. Induction curing is facilitated when the material to be heated has both a high power factor and a high dielectric constant, but high electrical conductivity of appreciable amount is not essential to the application of the method.

In this process, high conductivity is required, the electrodes must be in actual mechanical and electrical contact with unvulcanized material, and either direct current or alternating current, preferably 60 cycles or other common low frequency current, can be used. Furthermore, vulcanization by induction is not readily adaptable to mould cures, whereas vulcanization by conduction is readily adaptable to cures in molds under pressure.

It has been found in recent years that rubber, which is normally considered an insulator, can be rendered conducting or semiconducting by incorporating carbon black or other special materials in the composition. By this method of compounding, the resistivity of rubber can be reduced from the order of 10^{15} ohm-cm. to 10^2 ohm-cm. or less. As the resistivity decreases, it becomes increasingly possible to heat blocks of rubber by applying a moderate potential to two points or surfaces. The resultant current generates heat after the

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manner described in the previous paragraph. Such conductivity is characteristic of a given composition, both in the vulcanized and unvulcanized state. Under the latter condition, the heat generated by electrical means tends to cause vulcanization. If the temperature obtained by this means is sufficiently high and is maintained for a sufficient time, complete vulcanization results. The following is one of the possible conducting compositions of Neoprene:

Neoprene (Type GN)	100.0
Latac	0.3
Neozone-A	1.0
Extra light calcined magnesia	7.0
Acetylene black	50.0
Process oil	1.0
Zinc oxide	2.0

It has been found that a composition of the foregoing type can be vulcanized without difficulty in 10 to 20 minutes if sufficient electrical power is supplied. The power requirement depends on the shape and size of the sample to be vulcanized, but in experiments thus far, it has been found that power of 20 to 40 watts per cubic inch can be employed. An elementary set-up to illustrate this method of vulcanization is given in Figure 1. The vulcanized

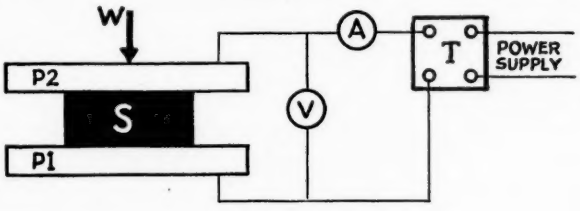

FIG. 1.

sample S is held between two platens P1 and P2 by the force W. Voltage across these platens is adjustable by means of the autotransformer or potential divider T, and the power supplied is determined by multiplying together the readings obtained from the voltmeter V and the ammeter A.

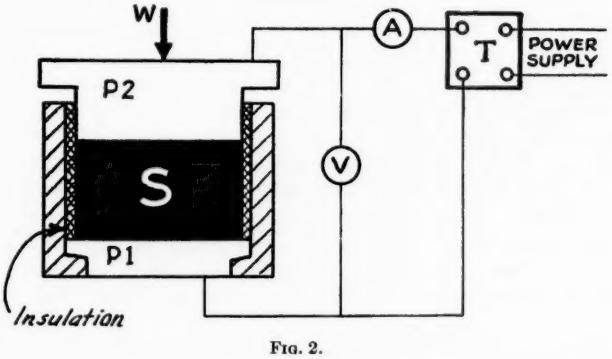

FIG. 2.

Figure 2 illustrates the logical extension of this system to the vulcanization of rubber under pressure in a mould. The symbols in Figure 2 have the same significance as the symbols of Figure 1. In order that vulcanization in a mould

shall be effective, the passage of the current through the sample must be evenly distributed. To do this, it is necessary that there be no possibility of shorting the current around the sample. For example, in vulcanizing a cylinder by this method it would be necessary to insulate the inside cylindrical surface of the mould. The potential would then be applied between the cover and the bottom of the cylinder. This can either be done by constructing a mould with insulating walls or wrapping the outside surface of the blank with an insulator—paper, for example.

More complicated shapes might require a very special mould construction and design of the part to be adaptable to this type of curing. However, a large proportion of mechanical goods is relatively simple in geometrical design and is readily adaptable to the curing system described.

This system of vulcanization differs in a basic way from curing methods now employed. It is apparent, from the description, that heating by electrical conduction produces the highest temperature at the innermost points of the specimen being cured. The temperature rise, therefore, occurs most rapidly at the center and the temperature gradient is from the inside out. In normal methods of cure the mould is heated and the specimen is vulcanized by conduction of heat from the outside inward. As a result of this, it is frequently difficult to obtain uniform cures throughout the mass, particularly if the cures are short or the specimens are large.

Whereas customary methods of curing vulcanize from the outside inward so the inner portions are relatively undercured, the proposed method vulcanizes from the inside outward, leaving the boundary regions relatively undercured. It is known that overcured rubber does not resist fatigue and cracking caused by flexing so effectively as rubber given a normal cure or undercure. For this reason a secondary advantage of conduction curing is a more favorable surface condition for resistance to fatigue and flex-cracking. A further advantage of heating from the inside, as in conduction curing, is that back-rinding at the closure of the mould is reduced, thereby producing superior articles and greater economy of production.

A high degree of uniformity in a cure should be obtained by combining the proposed method of vulcanization with present conventional methods. Moulded goods, as a class, are expensive. A large part of this expense is due to the time required for vulcanization. Vulcanization by conventional methods must permit adequate time for the temperature to become reasonably uniform throughout the volume of the sample. It is not practical, therefore, to shorten the length of time to any great extent by using high mould temperatures since this procedure accentuates the difference between the surface cure and the internal cure of the specimens.

However, by combining the proposed method with the conventional method, the internal temperature of specimens can be brought up to the mould temperature rapidly. It is therefore possible that much higher mould temperatures can be used, and that great economies in the time of vulcanization can be effected. This proposal also tends to make practical the vulcanization of much larger objects from rubber than has heretofore been considered practical.

When this method is employed in combination with conventional curing, it is not necessary in most cases to maintain electrical power after the inside of the specimen has attained the required temperature. This makes it practical to employ this method of heating at an early stage in a cure to bring the volume of the specimen up to the uniform temperature and to rely, thereafter,

on auxiliary equipment to maintain this temperature over the required length of time.

In the foregoing, ideal conditions have been assumed for illustrative purposes. In many actual cases, however, it will be found that curing by conduction is unstable, and that non-uniform cures may result, due to non-uniform distribution of current through the volume of the material being heat-treated. This can occur readily if one portion of the volume becomes hotter than surrounding regions. In this case the hotter portion requires lower volume resistivity, due to the temperature coefficient of resistivity. The current density increases accordingly, greater heating results, and the local temperature rise rapidly accelerates out of control. This tendency can be counteracted by incorporation of a ballast phase in the composition. This would consist of a material, electrically conducting at elevated temperatures, and of such physical form as to migrate down a temperature gradient.

Under conditions of non-uniform temperature distribution, the ballast phase would diffuse from the hotter regions to cooler regions at a rate dependent on the temperature gradient. The reduction in the concentration of the ballast phase in the hotter regions would reduce the conductivity and the temperature. On the other hand, addition of the ballast phase to cooler regions increases their conductivity and, as a consequence, their temperatures. Migration of a solvent has been demonstrated in experiments with toluene. Other substances show similar diffusion.

ACKNOWLEDGMENT

The foregoing was prepared as a confidential memorandum for the Rubber Chemicals Division, E. I. du Pont de Nemours & Co., Inc. The principles of the method were confirmed by a few tests in the Rubber Laboratory, but practical development has not been attempted. The author is pleased to acknowledge release of the report by the du Pont Company for publication. Jointly with them he expresses the hope that practical work may develop in the future to realize the advantages that seem to be promised.

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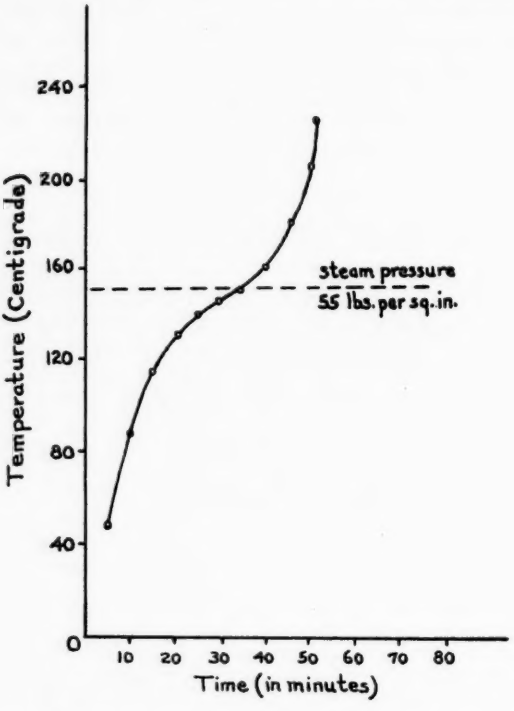
VULCANIZING OF EBONITE

CONTROLLED CURING OF NATURAL AND SYNTHETIC RUBBER EBONITES OF LARGE CROSS-SECTION *

N. G. QUINN

The vulcanizing of ebonite, particularly of large blocks or bars of substantial cross-section, has long been a source of production difficulty. The tendency of such vulcanizates to develop porosity or even more serious gassing has always necessitated a prolonged curing period at a comparatively low temperature. Improved compounding technique has greatly accelerated the curing process, but the period is still excessive and production is impaired.



The proposed method of control enables a higher curing temperature to be used, with a consequent considerable reduction in curing time; it further makes possible the use of stocks which previously could not be satisfactorily cured at all above a certain thickness.

The cause of internal gassing is generally considered to be due to the exothermic nature of vulcanization, the heat from which, in a large specimen, cannot be dissipated through the poorly conducting mass before a form of

* Reprinted from the *India-Rubber J.*, Vol. 105, No. 3, pages 62–63, July 17, 1943.

decomposition takes place. Temperatures as high as 250° C have been recorded in the centre of a 2 inch diameter bar while being press-cured at 150° C. By means of a needle thermocouple, the heat rise and reaction temperature at the centre of various vulcanizates have been observed and recorded; from these data a simple method of control has been found. The accompanying diagram shows a typical temperature record of the centre of a 2 inch diameter Neoprene ebonite bar cured in an autaoclave at 55 lbs. per sq. in. steam pressure. If no attempt is made to control the curing, the sample will burst in about 45 minutes. It is seen from the record that the initial rise follows a normal conductivity curve until a reaction point is reached. Thereafter a violent heat increase is observed, which, if not checked, inevitably damages the vulcanizate. Tests generally have been confined to a Neoprene type of ebonite of empiric composition. Natural-rubber ebonites have given consistent results, but a Neoprene ebonite was found to be particularly difficult to cure in large masses, for a minimum temperature was observed below which the vulcanizing reaction could not be initiated, however prolonged the curing. Above this temperature, without control, porosity, or even bursting, resulted before the mass could be homogeneously cured.

The method of control, therefore, is to apply ample heat to the curing pan in the first place; to take periodic readings—which should be plotted—of internal temperature; to check the applied heat as soon as the reaction rise is observed in a change of the plotted slope; to reapply "reaction point" heat as soon as the internal temperature has fallen below this value. When the first reaction rise has been safely checked, there is little difficulty in keeping the temperature at the necessary constant value, so that vulcanization will proceed in a normal cycle.

The reaction point will be found to vary with the mix, but a batch of similar articles can be controlled by recording the temperature of a pilot, provided the usual precaution is taken to surround the articles with a material of roughly their own specific heat. The method, therefore, gives a simple form of manual control which might reasonably be applied to full automatic regulation.

HARDNESS TESTING OF VULCANIZED RUBBER

II. COMPARISONS OF READINGS OF VARIOUS INSTRUMENTS *

H. A. DAYNES AND J. R. SCOTT

INTRODUCTION

In view of the importance of hardness tests and the variety of instruments in every-day use for this purpose, it is obviously desirable that the relationships between the readings given by these instruments should be known. Some data of this kind have been given in Part I[1] and in a report describing the Rubbermeter[2], but as many new instruments have been introduced since then, and published information on the relation of their readings to those of other instruments is scanty, some experiments were undertaken to make good this deficiency.

It had been hoped to obtain for use in these experiments all the commonly used hardness testers of the static indentation type, but unfortunately this was not possible, and the tests had to be confined to the Pusey and Jones plastometer[3], the R.A.B.R.M. hardness gauge[4], the Schopper rubber hardness tester No. 638[5], the Shore durometer type A[6], and the Strachan piezomicrometer[7]. With each of these instruments tests were made on a selection of rubbers ranging from very soft to very hard, so that a curve could be drawn showing the relationship between the readings of any pair of instruments. In the case of instruments provided with two indenting balls of different diameters, tests were made with both balls.

EXPERIMENTAL

DETAILS OF INSTRUMENTS AND TEST METHODS

For complete descriptions of the instruments, reference may be made to the sources quoted above. Below are given only those essential details on which the readings of the instruments depend. All the instruments are of the type in which a ball or blunt pin is pressed into the rubber by either a dead load or a spring, and the depth of the indentation used as the basis of the hardness reading.

Pusey and Jones plastometer.—This uses a ball of 0.25-inch or 0.125-inch diameter under a dead load of 1 kilogram. The zero position, from which the depth of the indentation is measured, is the surface of the sample at the point where the ball rests on it before the 1-kilogram load is applied (at this stage the ball is under a small load of about 85 grams, due to the weight of the stem and a spring in the gauge[4]). The 1-kilogram load is applied and allowed to rest on the ball for 1 minute, during which time the table is gently tapped to overcome any friction in the gauge. The hardness reading, expressed as the depth of indentation in 100ths of a millimeter, is then taken.

R.A.B.R.M. hardness gauge.—This is similar in principle and method of use to the plastometer, except that the depth of the indentation is measured

* Reprinted from the *Journal of Rubber Research* of the Research Association of British Rubber Manufacturers, Vol. 12, No. 9, pages 94–98, September 1943.

from the surface of the sample immediately surrounding the place where the loaded ball presses upon it, and the ball exerts practically no pressure on the rubber before the 1-kilogram load is applied. The reading is the depth of indentation in 100ths of a millimeter.

Schopper hardness tester.—This uses a ball 10 mm. in diameter, under a dead load of 1 kilogram. The zero position is obtained as with the plastometer, but as in the R.A.B.R.M. gauge, the ball exerts only a negligible pressure on the rubber before the 1-kilogram load is applied. Readings are

TABLE I

HARDNESS READINGS

R.A.B.R.M.		Piezomicrometer		Plastometer			Schopper		
0.25 inch	0.125 inch	0.25 inch	0.125 inch	0.25 inch	0.125 inch	Durometer	5 sec.	30 sec.	60 sec.
6	9	...	...	...	...	97	...	...	...
8.5	13	...	...	...	...	95	...	...	...
13	20	...	...	...	...	92	...	...	...
16	23.5	...	...	...	...	90.5	...	...	...
18	24.5	17	23.5	17	21	89	...	...	...
18.5	29	...	...	...	...	88	...	...	...
19	28.5	...	...	...	...	89	...	...	...
19	30	18	28	19	26	90.5	...	...	...
19.5	...	...	...	17	...	...	...	15.5	...
21	...	...	...	21	...	...	...	19.5	...
27	40	...	...	...	...	83	...	...	...
32	...	...	...	29	...	...	...	25.5	...
40.5	...	...	...	39	...	...	...	35	...
50	...	...	...	...	...	71	...	...	...
55	78	...	...	...	...	65	...	...	...
56	80	...	...	...	...	65	...	...	...
59	...	...	...	55	...	...	...	50.5	...
64	89	61	87	65	90	61	...	...	...
67.5	...	...	...	...	...	...	...	54	...
69.5	...	...	...	66	...	...	...	60	...
77	111	...	...	74	102	58	60	62	63.5
78	109	71	95	74	99	58	63	64	65
86.5	121	...	...	82	110	55	68.5	70	70
87.5	...	...	...	...	...	...	...	70	...
88.5	126	81	112	84	115	53.5	71	73	73
98	142	92.5	127	94.5	127	49.5	77	79	80.5
118	...	...	...	111	...	...	...	96	...
124	180	114	162	117	160.5	42.5	95	97.5	101
134	202	122	180	127	175	42	97	101	106
138	198	...	...	129	179	39	109.5	110.5	113
152	231	...	...	144	197	36	117	121	123
154	231	135	203	142	194	35	116	118	122
164	248	149.5	220	153.5	210.5	32	126	128.5	134
168	264	...	...	160	221	32	130	134.5	136
204	303	185	290.5	191	265	29	156	161.5	168.5
231	...	...	...	...	...	...	172	179	185
278	...	243.5	389	250.5	358	21	183.5	199	*

* Beyond the maximum limit of the scale (200).

taken after the load has acted for periods of 5 and 30 seconds, and the table is not tapped during the time the load acts. The reading is the depth of indentation in 100ths of a millimeter. This method of testing, recommended by the makers, differs from that used with the plastometer, R.A.B.R.M. gauge, and piezomicrometer, owing to the shorter loading period and the absence of tapping. Extra tests were therefore made with the Schopper gauge, giving

a 1-minute period during which the table was tapped. The latter method seems preferable because when the table is not tapped the reading may be markedly altered by slight accidental jarring of the instrument or the table. As these various procedures gave almost identical results at readings below about 60, rubbers harder than this were tested only with the 30-second period.

Shore durometer.—This uses an indenting pin about 1.5 mm. in diameter, tapered to about 0.75 mm. at the end, which is flat. The pin is pressed into the rubber by a spring so adjusted that the pressure applied is less the deeper the indentation. The depth of the indentation is measured from the surface of the sample immediately surrounding the pin. Readings are shown on a scale graduated from 0 to 100, so that 0 represents an extremely soft material and 100 an infinitely hard material, *i.e.*, one on which the pin makes no indentation. In use the instrument is pressed on to the sample and the reading taken immediately.

Strachan piezomicrometer.—This is similar in principle and method of use to the plastometer, and the reading is again expressed as the depth of indentation in 100ths of a millimeter.

RUBBER SAMPLES

Tests were made with each instrument on about 15 rubbers, and in some cases additional rubbers were tested to provide confirmatory data on doubtful parts of the correlation curves. The form of test-sample was that normally used by the Association, namely, two superposed discs 45 mm. in diameter cut from press-vulcanized slabs about 4.5 mm. thick, so the thickness of rubber tested was about 9 mm.

RESULTS

Table I gives the hardness results, each figure being the mean of four readings. In Figure (*a*) the readings of each instrument with each size of ball are plotted (on vertical scales) against the readings of the R.A.B.R.M. gauge with 0.25-inch ball (horizontal scale) to show how closely the readings of the various instruments can be correlated. The R.A.B.R.M. gauge has been chosen as the standard of reference because the "hardness number" is preferably defined as the depth of indentation produced by a given load acting on a ball of given diameter, and a 0.5-inch or 0.125-inch diameter ball is most commonly used, although the American Society for Testing Materials have adopted a 3/32-inch ball with a 3 lb. load[8]. The R.A.B.R.M. hardness gauge was designed to give a reading complying with this definition, because neither of the other instruments using the 0.25-inch and 0.125-inch balls does so, owing to there being a small load on the rubber before the 1-kilogram load is applied[4].

To facilitate the interconversion of readings given by different instruments, or readings obtained with balls of different sizes, the chart shown in Figure (*b*) has been prepared. The scales for the various instruments and sizes of ball are so drawn that all readings, lying on any one vertical line are equivalent, *i.e.*, represent the same degree of hardness. Thus, a reading of 130 on the R.A.B.R.M. gauge with 0.25-inch ball corresponds to 193 on this gauge with 0.125-inch ball, 118.5 and 171.5 on the piezomicrometer with 0.25-inch and 0.125-inch balls respectively, 123 and 169 on the plastometer with 0.25-inch and 0.125-inch balls respectively, 41.5 on the Shore durometer, and 101, 103, and 105 on the Schopper gauge with 5, 30, and 60 second periods, respectively.

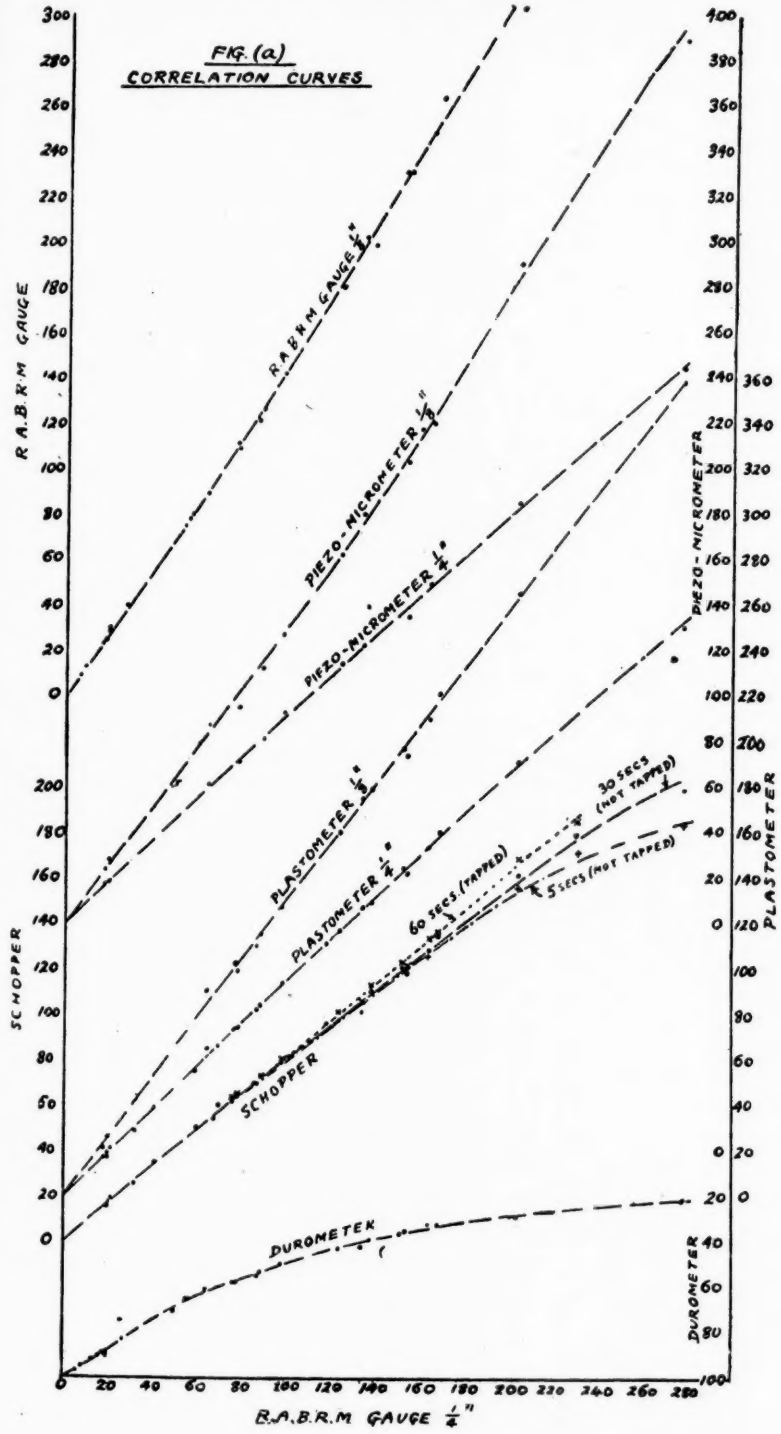


FIG. (a)
CORRELATION CURVES
R.A.B.R.M GAUGE
SCHOPPER
PIEZO-MICROMETER
PLASTOMETER
DUROMETER
R.A.B.R.M GAUGE ¼"
R.A.B.R.M GAUGE ½"
PIEZO-MICROMETER ½"
PIEZO-MICROMETER ¼"
PLASTOMETER ½"
PLASTOMETER ¼"
60 SECS (TAPPED)
30 SECS (NOT TAPPED)
5 SECS (NOT TAPPED)
SCHOPPER
DUROMETER
R.A.B.R.M GAUGE ¼"

FIG. (b) CONVERSION CHART

EQUIVALENT READINGS LIE ON THE SAME VERTICAL LINE

No attempt is made here to discuss the theoretical aspects of the relation between the hardness reading and the diameter of the ball or between the readings of different instruments, because it is intended to deal with these matters in a future report on the theoretical basis of indentation hardness testing. Two points may be mentioned, however. It has been stated[9] that the ratio between the readings with 0.125-inch and 0.25-inch balls on the plastometer is 6 to 5; the present results show, however, that it is very nearly 7 to 5, and the corresponding ratios for the R.A.B.R.M. gauge and piezomicrometer are of the same order, though exact figures cannot be given as the correlation curves are not straight. The ratio between the readings of the R.A.B.R.M. gauge and the plastometer, using 0.25-inch balls, is 1.08, which agrees approximately with that found in previous experiments[5].

SUMMARY

Tests have been made on numerous rubbers with the R.A.B.R.M. hardness gauge, the Strachan piezomicrometer, and the Pusey and Jones plastometer (using in each case ¼-in. and ⅛-in. diameter balls) and with the Shore durometer and Schopper hardness tester, to determine the relationships between the readings given by these instruments. The results are tabulated and represented graphically as correlation curves. A conversion chart is given by which the reading obtained with any one instrument or size of ball can readily be converted into the corresponding reading for any of the other instruments or sizes of ball.

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BONDING OF RUBBER TO METALS *

S. BUCHAN

Rubber has been used for many years as a medium for minimizing and absorbing mechanical vibrations. Until comparatively recently, however, its employment for this purpose has been limited by the practical difficulties encountered in uniting it successfully with other more rigid materials, such as metals. At this stage, technical development in the rubber industry fell short of engineering design and manufacturing requirements.

Earlier methods for uniting rubber to metal consisted either of attaching the rubber by mechanical means or by using a layer of ebonite between the soft rubber and the metal. These methods, however, were open to criticism, either on mechanical or chemical grounds, and the bond strengths were obtained at the expense of some of the flexibility of the units. Later, derivatives were produced by the action of sulfuric acid on rubber which gave excellent bonding properties, although they were thermoplastic and tended to weaken at temperatures over 60° C. Recently, cements based on rubber hydrochlorides have been put on the market which are superior in all respects to previous types. These are the "Ty-plys".

The production method for bonding rubber to metal by means of an intermediate layer of electrodeposited brass was developed in America between 1920 and 1930. The method was worked for some time as a semisecret process, and little information about the conditions employed was given in the technical literature.

When starting out to develop a process for obtaining direct adhesion of rubber to metal by means of a brass interlayer, the problem that faces the chemist is threefold: how to obtain a suitable brass deposit, how to compound rubber suitable for bonding, and how to develop and specify satisfactory processing procedure.

The brass-plating process.—Almost all metals and alloys can be brass-plated. The main difficulty lies in getting them to the requisite state of chemical and physical cleanness which is necessary to obtain a uniform and adherent electrodeposit. With some metals it may be necessary to deposit first of all a protective coating of another metal in order to minimize oxidation of the surface before brass-plating. In the case of nonferrous metals, too, the electrochemical couple set up between the metal itself and the brass deposit may lead to corrosion of the base metal. This is an aspect which must be considered, bearing in mind the service conditions under which the unit must ultimately function.

Iron or steel parts are first degreased either by means of organic solvents, followed by boiling in aqueous degreasing solutions, or merely by means of the latter. Following this, all rust, scale, etc., is removed from the surface of the metal by immersion in either dilute or concentrated acid. Degreasing in aqueous solutions and acid treatment are usually facilitated by the passage of electric current, the metal parts forming either the anode or cathode, depending on the process and the procedure employed.

* Reprinted from the *Transactions of the Institution of the Rubber Industry*, Vol. 19, No. 1, pages 25–38, June 1943.

When thoroughly cleansed, the metal parts are hung on the cathode rods of a brass-plating bath, in which the anodes consist of sheets of brass, the composition of which is, usually, 70 parts of copper to 30 of zinc—although the writer has used anodes of a 80/20 ratio equally successfully. The plating solution consists essentially of a mixture of copper and zinc cyanides in sodium or potassium cyanide. The actual plating conditions, time, current density, temperature, etc., have to be found out by experiment for each solution.

The bath itself should be analyzed frequently, and should be corrected by the addition of chemicals to keep its composition always within narrow specified limits. The deposit itself should be checked often as it is the brass layer which decides ultimately the success or failure of the bond. Chemical control at this stage is essential.

After plating, the metal parts pass through washing and drying baths to the inspecting and cementing departments, and eventually pass to the building section for assembling with the rubber.

Compounding for adhesion.—Care must be taken in the choice of compounding ingredients for rubber qualities designed for bonding to metals, not only from the point of view of their chemical purity, but also on account of the desirable properties, especially as regards adhesion, which they may confer. The method of compounding and the function of the various ingredients are the same as for standard qualities, but the choice and the range of some of the essential compounds are limited. The use of sulfurless mixings is prohibited; the use of fast accelerators is restricted; certain fillers are unsuitable. Earlier experiments indicated clearly that a good quality of smoked sheet rubber was superior to other more inferior grades containing higher proportions of acetone-extractable substances. At the same time it was found that aging of the raw rubber did not improve the bonding properties of the mixed stock. These original tests were mainly qualitative, but the results are trustworthy and have not been repeated. In the following series of tests, the effects of the method and degree of mastication of the raw rubber have been studied quantitatively.

The general method of carrying out these tests was as follows. The raw rubber was processed as required, its plasticity and recovery measured, to ascertain the degree of mastication reached, and the rubber was then used for mixing a standard rubber quality (AD. 27) which was known to give a good bond with brass-plated steel. At the same time some of the AD. 27 was let down as a cement and used for painting over the bonding surfaces of the brass deposit.

The units used for testing purposes consisted of two concentric rings, bonded together by means of the rubber under test, as shown in Figure 1. The unit was tested in shear. To reduce the possibility of inconsistencies due to the human element, introduced during building, all were vulcanized by means of an injection mould, which eliminates entirely the need for building and assembling.

In Experiment 1, the raw rubber was warmed at 70° C for 30 minutes and then sheeted on warm rolls (70° C). The rubbers in Experiments 2 to 5 inclusive, were ground through a very close nip with the rolls kept cool throughout. After grinding, the rubbers were sheeted, as in Experiment 1, on rolls maintained at 70° C.

The hot-masticated rubber was taken from a 250-pound factory batch,

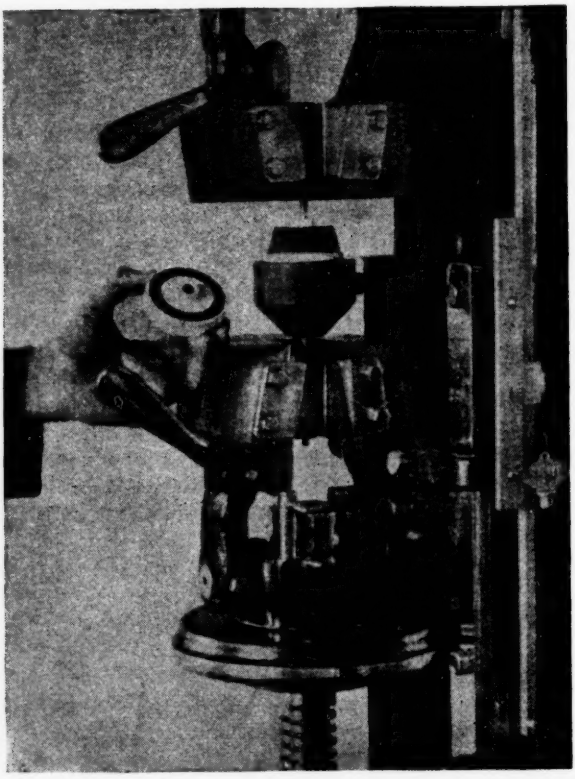

FIG. 1.—A test unit under load.

which was mixed, under supervision, on a No. 9 Banbury to the following specification:

Banbury (all water off) 14 minutes.
Temperature as rubber leaves the machine, 380 to 390° F.
Mill (cold rolls)

Grind at once	12 minutes
Open to 5/8 in. and blend	8 minutes
Cut off	6 minutes
Total	26 minutes

In Experiments 7 to 9 inclusive, the mill rolls were heated to 120 to 125° C, and the softening agents blended in thoroughly. The batches were then ground 10 times on hot rolls to ensure proper dispersion, and sheeted.

Plasticity and recovery readings were taken on samples of raw rubber and AD. 27 batches, all mixed as nearly as possible to the same cycle specification. Before making the bonded test-pieces, determinations were made on the mixed qualities of their rates of set-up. Some results obtained are shown in Table 1.

The two main findings were: (1) that bonding strength is independent of the rate of set-up of the rubber, which diminishes with increased mastica-

tion, and (2) that increased mastication of the raw rubber does not materially assist the bonding properties of the mixed rubber quality.

It will be observed, too, that certain chemical softeners can be used for plasticizing purposes without apparently affecting the bond strength adversely.

The most important compounding ingredient from the point of view of bonding appears to be sulfur. Mixings with no sulfur present give no adhesion to metal; mixings with high sulfur contents, such as unaccelerated mixings, give consistently good adhesions, whereas mixings with moderate percentages of sulfur with organic accelerators give variable adhesions. In accordance

TABLE 1

	Raw rubber		Mixed rubber		
Method of mastication	Plasticity (Williams P.P.) (mm.)	Recovery (mm.)	Plasticity (mm.)	Recovery (mm.)	Adhesion (lbs. per sq. in.)
(1) Unmasticated	5.82	0.353	2.42	0.098	866
(2) 10 grinds	5.00	0.210	2.50	0.098	862
(3) 20 grinds	4.44	0.160	2.20	0.070	905
(4) 30 grinds	3.72	0.078	2.10	0.070	865
(5) 40 grinds	3.00	0.065	2.04	0.076	804
(6) Hot masticated	4.00	0.220	2.48	0.062	918
(7) 0.25% R.P.A. No. 2	3.40	0.160	1.80	...	1047
(8) 0.25% R.P.A. No. 3	2.30	0.165	1.70	...	827
(9) 0.50% R.P.A. No. 3	2.25	0.140	1.80	...	851

with modern practice, mixings for bonding purposes usually contain only moderate quantities of sulfur; other ingredients, including the accelerator, are modified to give the maximum degree of adhesion combined with the other required properties. By this means it is possible to produce rubbers which are the equal of nonbonding rubbers in all their physical properties and have, also, exceptionally high bonding strengths. Sometimes it is not convenient to have sulfur above a certain percentage present in a bonding rubber; when this is the case, the addition of small proportions of either selenium or tellurium gives good results. The utilization of sulfur in nascent form has been tried also and the adhesion has been most promising.

When organic accelerators are used in mixings, it is fairly obvious that the rate of set-up and cure of the mixings produced, as well as any purely chemical action produced by the accelerators themselves, must have some affect on the bonding properties. It has been observed that, although excellent adhesion can be obtained using accelerators such as mercaptobenzothiazole, more consistent results are obtained by using accelerators either slower in action, such as hexamethylenetetramine, or the delayed action type. Because of the many advantages gained in processing by using delayed-action accelerators, most of the experiments described have been carried out with this type.

Although it is advisable to use accelerators with delayed actions; the bonding properties do not depend in any way on the amount of retardation. Indeed it has been found that, although delayed action up to a point is beneficial, if carried too far it may prove to be disadvantageous. Figures 2 and 2*a* show the rates of set-up and cure of two mixings AD. 20 and AD. 27, and, although on inspection it might be thought that AD. 20 would prove to be the better bonding quality, such is not actually the case. Moderate retardation at the

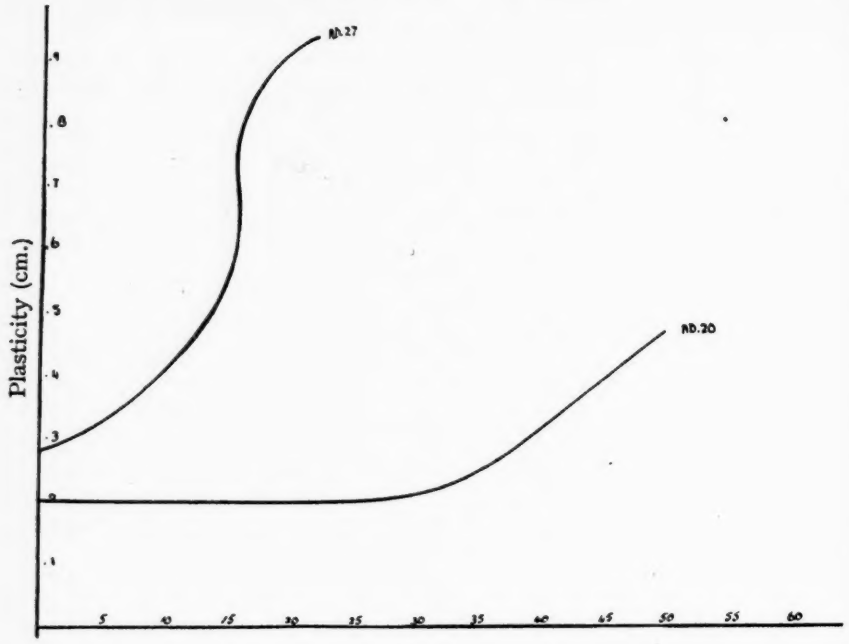

FIG. 2.

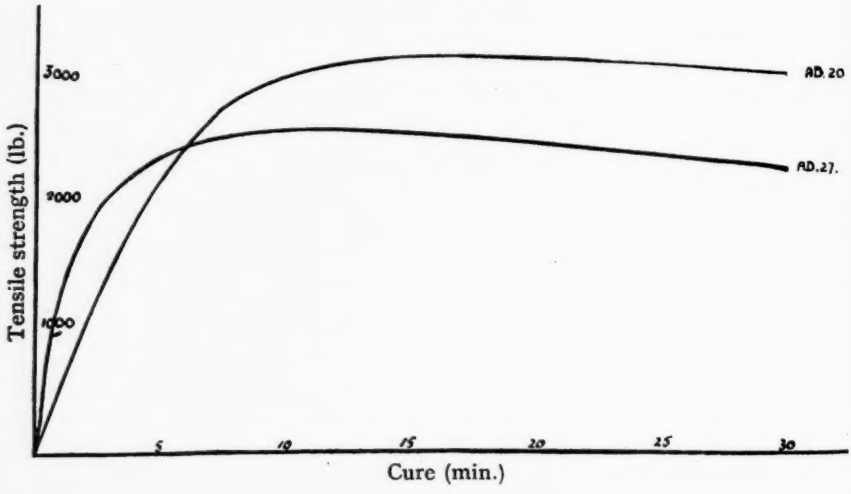

FIG. 2a.

commencement of the cure appears to be an advantage, but once vulcanization starts it should not be long drawn-out. If possible the cure should be regulated so that vulcanization occurs as evenly as possible throughout the rubber mass; otherwise surface vulcanization may occur on the bonding surfaces while the rest of the rubber is still in a mobile state. If this does occur, the

rubber surface next the brass may not have long enough in intimate contact with the bonding surface for adhesion to develop. Table 2 indicates the degree of adhesion that can be expected from various accelerators. In all tests, a cement of each rubber being tested was let down in solvent and applied to the bonding surfaces before applying the rubber by injection.

TABLE 2

Accelerator			Adhesion (lbs. per sq. in.) on inner ring after cure of 25 min. at 307° F	
Trade name	Chemical constitution	Wt. per 100 lbs. of raw rubber		Remarks
M.B.T.	Mercaptobenzothiazole	12 oz.	900	
Z.M.B.T.	Zinc salt of M.B.T.	12 oz.	1,015	
M.B.T.S.	Dibenzothiazyl disulfide	12 oz.	780	
D.P.G.	Diphenylguanidine	12 oz.	485	
Vulcafor DA.	M.B.T. 30% + D.P.G. tartrate 70%	12 oz.	860	
Ureka	Dinitrophenylester of benzothiazole & D.P.G.	12 oz.	708	
Ureka White	...	12 oz.	752	
Ureka D.D.	...	12 oz.	700	
L.P.D.	Lead pentamethylenedithiocarbamate	6 oz.	424	
C.P.D.	Cadmium pentamethylenedithiocarbamate	8 oz.	147	
Z.N.P.D.	Zinc pentamethylenedithiocarbamate	4 oz.	171	
T.M.T.	Tetramethylthiuram disulfide	4 lbs.	Nil	No sulfur
T.M.T.	Ditto	2 oz.	137	Sulfur present

The master batch employed was AD. 27 without accelerators, which were added in the proportions shown.

It has been observed that alteration of the temperature of cure has apparently very little effect on the consistency or ultimate strength of the bond; also, that undercure or overcure only slightly affects adhesion. To verify this and to put the results on a quantitative basis, test units built with the same rubber were cured for varying lengths of time so as to give both under and overcured rubbers. The results (Table 3) indicate that state of cure is not

TABLE 3

Time of cure of AD. 27 at 307° F	Adhesion calculated on inner ring (lbs. per sq. in.)	Free sulfur on 100 parts rubber	Remarks
10	760	0.714	
15	827	0.691	
20	800	0.454	
25	804	0.104	Optimum cure
30	1,014	0.062	
35	1,020	0.054	
40	997	0.048	

a critical factor in deciding bond-strength. When the undercures or overcures are such that the properties of the rubber, such as tensile strength, tear-resistance, etc., are badly affected then the bond strength will show signs of falling off.

McCourtney[1] stated that the presence of antioxidants in bonding rubbers could affect appreciably the adhesion obtained. Qualitative tests carried out

some years ago indicated that antioxidants such as Agerite powder, Nonox, B.L.E. and Flectol-B, had little affect on the bonding properties of rubber and, again, the experiments outlined below were carried to give quantitative confirmation. It will be seen from Table 4 that the antioxidants tested appear

TABLE 4

Antioxidants		Parts added per 100 parts raw rubber	Adhesion (lbs. per sq. inch) on inner ring	Remarks
Trade name	Chemical constitution			
Nil		0	850	
Agerite powder	Phenyl-β-naphthylamine	1	860	
Ditto	Ditto	2	998	
B.X.A.	Ketoneamine condensation product	2	842	
Nonox-S	Condensation product of aldol-α- and aldol-β-naphthylamine	2	853	
Vulcaflex	Dimethoxydiphenylamine	2	601	Probably badly dispersed
B.L.E.	Ketoneamine reaction product	2	913	
Flectol-A	Polymerized 2,2,4-trimethyl-1,2-dihydroquinoline	2	836	
Santoflex-B	Reaction product of acetone and para-aminodiphenyl	2	705	
Santoflex-BX	Santoflex-B with diphenyl-para-phenylenediamine	2	800	

to have had no real influence on the bonding characteristics of a given rubber. Again AD. 27, with the antioxidant omitted, was used as a master batch.

It has been emphasized by some bonding experts that softeners which tend to bloom to the surface of rubber are not suitable for adhesion. Where such stocks are used in an injection mould, however, surface blooming does not matter, as no prepared rubber surfaces are placed against the brass. Moreover, if standard moulding procedure is adopted, it is usually necessary to clean the rubber surface with a solvent such as benzene before applying it to the brass. Provided, therefore, that the rubber-metal unit is vulcanized fairly soon after it is assembled, as it should be, the presence of a blooming softener should not adversely affect bond strength more than any other. Only a few of the more commonly used softeners were tested (see Table 5), each of them

TABLE 5

Softener	Parts added on 100 parts raw rubber	Adhesion (lbs. per sq. in.) on inner ring
Master batch	Nil	860
Mineral rubber	5	854
Vaseline	5	1,117
Parraffin wax	2	913
Plastogen	5	859
Stearic acid	5	892
Pine tar	5	900

being added in turn to a master batch of AD. 27 which already contained 5 per cent of mineral rubber and 3 per cent of stearic acid.

From these tests it would appear that the addition of softeners in reasonable quantities does not affect the bonding properties of a rubber. Chemical

softeners such as thio-β-naphthol do not effect adhesion adversely, as has been shown earlier.

Various fillers, mainly of the reinforcing type, have been examined from time to time to determine their effect on bonding. Among the carbons, channel black, although it can give high adhesion figures when incorporated in suitable mixings, tends to give rather variable results. This erratic behavior is probably connected with its high surface activity and its tendency to absorb materials which may or may not injure adhesion. Softer blacks, such as Gastex or P-33, can be incorporated without detriment, and inert blacks, such as Thermax, make excellent filling ingredients.

Another good black is lampblack. In moderate quantities it appears to benefit adhesion, although at the same time it increases the rates of set-up and cure of the rubber. Zinc oxide, too, when used as a reinforcing filler gives excellent bonding characteristics to rubbers, although its very high specific gravity rather limits its use. Other fillers which can be used are clays, kieselguhr, whiting, and fat acid-treated whitings. Inert filling ingredients for the most part have not been examined, but most of them can probably be used without difficulty.

Most production-scale bonding with synthetic rubbers has been carried out to date with Neoprenes (types E, G, GN, and Z). The normal type of mixing does not give very good bonding properties, but mixtures can be made which will give good and consistent adhesion. From the point of view of consistency, Neoprene-E has been found to be best, with G and Z good seconds. The presence of sulfur has been found to be advantageous, even if only present in minute traces. Bond strengths on test units have been obtained with Neoprene-G of over 1,200 lbs. per sq. in., but it is interesting to note that this quality had to be withdrawn from production because it scorched too readily. Hycar-OR, Perbunan-extra and Buna-S have all been tested for adhesion to brass and found to give satisfactory qualities. Thiokols have not been bonded to brass, but work on this synthetic material has not been pursued with the same energy as the others because of its mechanical shortcomings.

General processing.—All brass-plated metal parts should be examined by an inspector, preferably attached to the laboratory, to ensure that the brass comes up to specified standards, irrespective of the needs of production. The usual visual defects found on electrodeposited brass are bad color; watermarking; loose, powdery or blistered deposit; and staining due to occluded chemicals, rusting of base metal, etc.

From the color of defective brass, it is often possible to diagnose fairly accurately what is wrong with the plating bath, although addition of chemicals must not be made without first verifying by either bath or plate analysis that these are required.

In some metals and alloys, such as cast iron or admiralty gun-metal, porosity may be encountered fairly frequently. The solutions employed in the cleaning and plating baths are occluded in the pores of the metal and cause staining of the brass deposit after it leaves the plating bath (see Figure 3).

The mixing, calendering and extruding of rubber for bonding are performed in the same manner as for normal rubber qualities. It is, perhaps, rather more important that dispersion of the compounding ingredients should be thorough and that no surface scorching should occur in calendered or extruded rubber. As soon as building-solvents have had time to evaporate off or disperse into the rubber, the composite rubber-metal unit should be vulcanized.

Oxidation of the brass surface, although not necessarily always fatal, should be given as little opportunity to develop as possible.

Mouldings of the rubber-metal unit can be carried out either in the standard type of mould or in the injection type. Both can give excellent results and can be used as circumstances dictate. When delayed-action accelerators are used, little or no advantage is gained by using low temperatures. The effect of pressure during moulding on the strength of the bond is rather apt to be

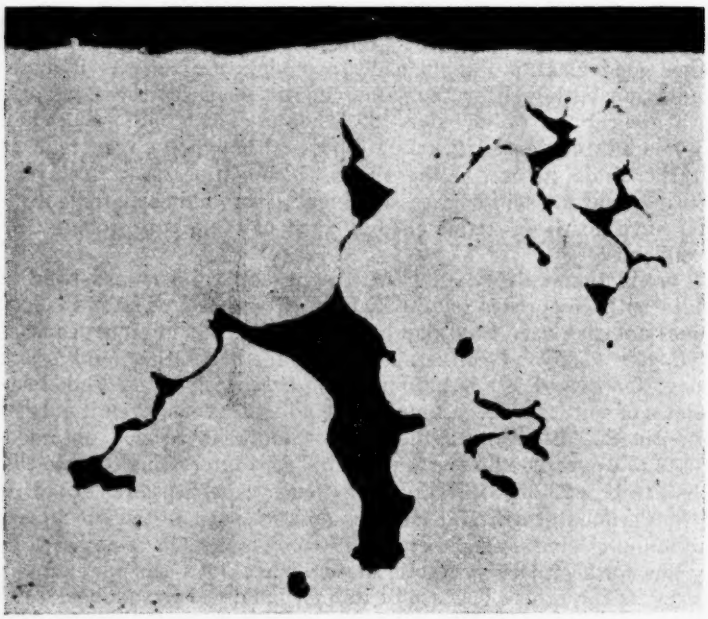

FIG. 3.—Photograph (magnified × 150) of section through a gun-metal flange, showing the type of porosity that may be encountered. The cavities are connected to the bonding surface by means of minute cracks through which the cleaning and plating solutions exude.

overestimated. Provided that the mould is kept closed and that sufficient pressure is applied to press the rubber into intimate contact with the brass deposit then that appears to be all that is necessary. Higher pressures produce no appreciable increase in bond strength. It is possible to cure some rubber-metal units only partially in moulds and then to complete vulcanization in open steam. Table 6 gives comparative figures obtained on units which had

TABLE 6

Adhesion (lbs. per sq. in.) after curing at 307° F in		
Mould (25 min.)	Mould (10 min.) open steam (15 min.)	Mould (15 min.) open steam (10 min.)
1,165	1,024	1,054
1,268	978	1.156
1,230	940	1,166
1,174	978	1,078
1,278	987	1,187

their full cure in a press and on others which were partially cured in a press and then finished in open steam.

However rigid the process and rubber control is in a rubber bonding plant, it should be recognized that 100 per cent efficiency cannot be maintained. Because of the great number of variables, cases are bound to occur of partial or total bond failure. The greater the degree of control exercised, of course, the fewer will be the number of failures. This being the position, it is essential that all bonded parts should be tested in such a way that those with sub-standard bonds can be detected and removed before units are despatched from the factory. As far as possible, the test should duplicate the most stringent conditions which the units will have to meet in service.

PROPERTIES OF THE RUBBER–METAL BOND

In any rubber-metal unit, the part which is most open to suspicion is the bond. When the bond is obtained by means of brass-plating, the efficiency of the adhesion under certain conditions appears to be still more distrusted,

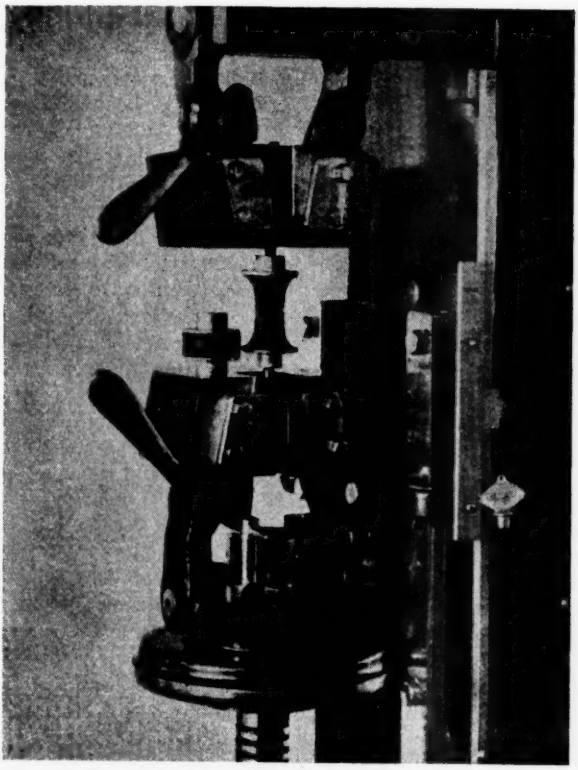

FIG. 4.—A mounting under tension compared with an unstressed mounting.

and it is intended in this section to discuss both the merits and demerits of the rubber-to-brass method of bonding.

The strength of the bond is regarded as being of paramount importance, and this aspect will be dealt with first.

In pure tension (see Figure 4), a rubber quality of 40° to 65° Shore hardness,

without addition of inert diluents, can give at room temperatures ultimate bond strengths of from 800 to 1,300 lbs. per sq. in. before falling. It might be stressed here that, when failure occurs at these high figures, the bond should not be regarded as being faulty because it may fail on the metal surface and not by tearing through the rubber. Failure of the bond by rubber failure instead of by separation at the metal can always be made to occur by weakening the tear resistance of the rubber, and this method of evaluating bond-strength must be viewed with a certain amount of suspicion. In shear the ultimate breaking stress is usually of the same order as that obtained under tension, as the results quoted earlier showed. Under compressive forces the bond-strength is high, and loadings of the order of 10,000 lbs. per sq. in. have been applied without ill effect. When loading in compression, the limiting factor is more the degree of permanent set that may occur in the rubber rather than the possibility of bond failure. This is especially the case with synthetic rubbers. In torsion, the rubber component can be deflected through a large angular displacement without the bond being affected. In one coupling, which measured roughly 3 inches internal diameter, 6 inches outside diameter, with an average length of 3 inches, the rubber was stressed repeatedly under a force of over 3,000 foot-pounds and an angular deflection of over 300° was obtained. This coupling, although seemingly a freak case, has been put on service tests and has functioned successfully (see Figure 5).

Finally, there is stripping adhesion to be considered. This consists of cutting the rubber down to the metal along two parallel lines and stripping off the rectangular strip of rubber between. When a piece of rubber one inch wide is pulled off, say, a tank-wheel, the bond strength recorded may be as high as 300 to 400 lbs. per in. width. In Specification Tanks 3A, the minimum adhesion of treads to wheel is given as 50 lbs. per in. width. In making load-deflection tests, whether in tension, shear, compression or torsion, the dimensions of the rubber under stress have a considerable bearing on the results obtained. The ratio of the free surface-area to the stressed area, known as the freedom ratio, must therefore be considered.

Ultimate bond strengths of the order indicated have been obtained also on brass, aluminium, aluminium alloys, stainless steels and so on, and they appear to be independent of the nature of the underlying metal, provided that the brass deposit can be made to adhere effectively. Adhesions of the same order have been obtained, too, with Neoprene-E, -G, -GN, and -Z, Perbunan, Buna-S and Hycar-OR.

Quantitative tests carried out under dynamic conditions on bonded units have borne out results obtained under service conditions. The rubber-metal bond does not fail readily under reasonable loadings, even when vibrated and flexed simultaneously. Hundreds of thousands of bonded units continually in use as mountings, couplings, etc., most of them functioning dynamically and the almost negligible percentage of failures confirm this statement.

An impression seems to be prevalent that it is not possible to compound rubber for bonding purposes with low permanent set characteristics. This is not the case. Bonding rubbers are being compounded and used successfully in which the permanent set properties compare favorably with nonbonding stocks. In the same way bonding qualities need show little hysteresis loss.

The resistance to heat of the rubber-brass bond is good. Up to 150° C, the type of failure is the same as that obtained at normal temperatures. The ultimate strength of the bond falls off with rise in temperature, but this can be due only to the lessening of the tensile properties and tear-resistance of the

rubber at elevated temperatures, as there appears to be no tendency for failure to occur actually on the metal itself. At lower temperatures the bond strength increases considerably. Similar results were obtained when natural rubber was replaced by Neoprene.

Although the presence of copper in contact with rubber causes it to depolymerize and revert, there appears to be no tendency for brass to affect

FIG. 5.—Rubber-metal coupling. Two concentric sleeves bonded together with rubber.

bonding rubber qualities in the same way. Samples of rubber bonded to metal have been shelf-aged for five years, and the bond after this time appeared to be unaffected. Similar results were obtained when rubber-metal units were subjected to accelerated aging tests at 90° C in a Geer oven.

When rubber-bonded-to-metal parts have been immersed in aviation spirits, lubricating and fuel oils, both at room temperatures and at 70° C, the rubber was attacked but the bond itself remained essentially unaffected. Again, when Neoprene was substituted for rubber, the bond was again unharmed; the

Neoprene stock, of course, showed a higher degree of resistance to heat and oil than the rubber one.

Certain chemicals tend to attack the bond, some because of their solvent action on the brass. In this category may be included ammonium persulfate in ammoniacal solution, nitric acid, trichloroacetic acid, etc. Cretain solutions at boiling point seem to be fairly effective in this way, *e.g.*, a boiling solution or suspension of lime. This aspect of rubber-to-metal adhesion is important.

The nature of the rubber-to-brass bond has been studied qualitatively for some time, and the results obtained have been most illuminating, but this most intriguing problem still calls for much detailed research before the reactions involved are fully settled.

ACKNOWLEDGMENT

Acknowledgment is made to the Directors of the T. B. Andre Rubber Co., for permission to read and publish this paper.

REFERENCE

[1] McCourtney, *Vanderbilt News* **3**, 8 (1933).

SETTING-UP OR SCORCHABILITY TEST OF COMPOUNDED RUBBERS *

F. B. MENADUE

Tests already described for determining setting-up or scorching make use of a plastometer[1] or sheeting from a mill[2]. The following method has been designed for sensitivity and for simplicity in preparation of the test-piece to be used for both routine tests and research, and is of particular value in enabling a definite figure of measurement to be quoted.

The specimen of rubber (about ¼ inch thick, 3 inches long and 1 inch wide) taken from the mill batch is heated in water for a predetermined time and temperature. Test strips, $\frac{5}{32}$ inch × 2½ inches × the original thickness, are cut from it, thus exposing smooth, flat internal surfaces. These strips are bent over a metal plate $\frac{1}{16}$ inch thick, with the internal cut surfaces at a right

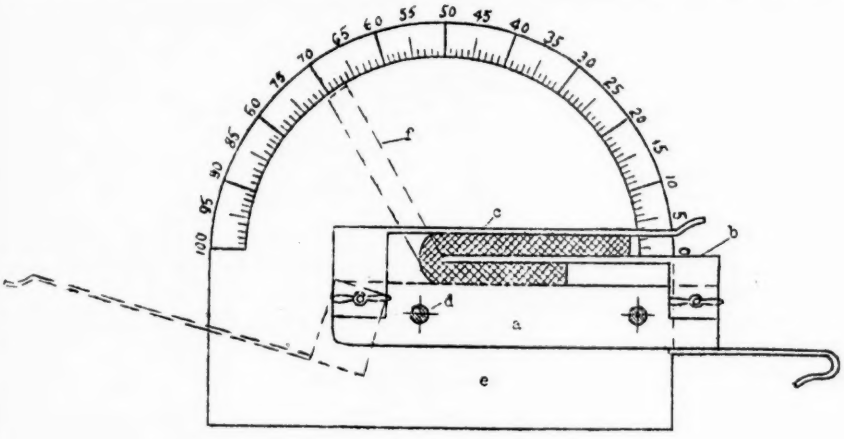

FIG. 1.

angle to the bending plane and thus in contact with the plate surfaces; are heated for 2 minutes at 210° F; then one arm is released, and the amount of its recovery at 2 seconds and at 60 seconds is noted.

In the diagram, (a) is the base of wood or grooved aluminum ½ inch wide; (b) is a two-shouldered hinged plate to hold down one arm of the test-piece, and (c) another one to hold the other arm. Thumb-screws hold the plates tight. The whole is heated in water for 2 minutes at 210–212° F and is then placed in position over the graduated arc scale (e), using the pins and slot (d) as guides. The scale base is in a tray of water at 210° F, for otherwise the test-piece cools rapidly. Plate (c) is rapidly swung back, as shown by broken lines, and the position of the freed arm is noted. For routine control, the water tray may be dispensed with, the reading at 2 seconds being sufficient; or, to obtain the 60 seconds' reading, beyond which no further recovery takes

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place, the holder with the one arm of the test-piece free to move may be immersed in the water for 60 seconds, taken out, and read as above. (f) is the freed arm of the test-piece (showing recovery of 67 on the scale).

Since some rubbers behave differently in wet heat and in dry heat, and since setting-up or scorching concerns only dry-heat conditions, the original mill sample is protected at the point of bending during the scorching treatment in water; or is clamped in a light frame between thin metal plates.

The percentage recovery is calculated as the ratio of the reading, obtained as above, to the reading obtained from a sample vulcanized in a press to its optimum cure. The latter is that cure at which the rubber shows its maximum recovery under the test conditions described above.

Figure 1 shows a typical test, in which the rubber sample, after having been vulcanized for 1 hour at 212° F, showed after 2 seconds a recovery of 67, which was 73.6 per cent that of the maximum recovery of 91 of the same rubber vulcanized to its optimum cure of 10 minutes at a steam pressure of 70 lbs. per sq. in.

Table 1 shows the effects of different methods of inducing scorching with two different types of rubber mixtures, (A) and (B), and also the percentage recovery values after different times of release.

(A)		(B)	
Rubber	100	Rubber	100
Sulfur	1.5	Sulfur	2.75
Mercaptobenzothiazole	1.5	Diphenylguanidine	0.5
Di-*o*-tolylguanidine	0.25	Magnesium oxide	2
Oil	5	Stearic acid	0.5
Zinc oxide	10	Clay	40
Whiting	120	Whiting	40

The optimum press-cure of mixture (A) was 6 minutes at 70 lbs. per sq. in. steam pressure: in which case the maximum recovery was 88 after 2 seconds and 90 after 60 seconds. The optimum press-cure of mixture (B) was 10 minutes at 70 lbs. per sq. in. steam pressure; in which case the maximum recovery was 91 after 2 seconds and 93 after 60 seconds.

TABLE 1

Mixture	Time of preliminary heating to induce scorching at 212° F (min.)	Proportional recovery after release from bending: after 2 seconds	after 60 seconds
A	0	0	0
	10	0	0
	30	66	77
	45	70	83
	60	94	100
	160	94	100
B	0	0	0
	10	0	0
	30	0	0
	60	15	34
	90	29	55
	160	45	84

The results in Table 1 show the wide range of scorchability which may be encountered. The range and sensitivity are greater when the readings are taken at the end of 2 seconds, in that the rate of recovery plays a greater part,

and readings at this period of 2 seconds are recommended for general control work.

The boiling temperature of 212° F for inducing scorching of 1 hour is unduly high for tests of the tendency of mixtures to "set up" during bin storage, and these conditions can be modified as seems advisable. In determining the extent of set-up which has occurred in storage, no preliminary boiling or heat scorching is carried out.

It is obvious that before drawing any conclusions as to the processing characteristics and tendency to set-up or scorch of a rubber mixture, the plasticity must be taken into account in conjunction with the percentage recovery, or, to be more exact, the heat produced by friction and the conductivity.

Precision in the measuring technique, particularly the time and the temperature in the two-minute setting operation of the bent test-specimen, is essential. Recovery diminishes as the time of this heating operation is increased.

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[1] Weaver, *Rubber Age* (N. Y.) **48**, No. 2, 89 (1940).
[2] Anon., *Vanderbilt News* **8**, No. 5, 26 (1938).

INFLUENCE OF EXPOSING VULCANIZED RUBBER TO LIGHT ON ITS SUBSEQUENT AGING IN THE DARK *

J. R. Scott

When accelerated aging tests have been required to be carried out on vulcanized rubbers, such as for specification purposes, no strict requirements have hitherto been laid down concerning the conditions of storage of the samples or test-specimens after vulcanizing and prior to aging. Apart from avoiding heating or exposure to direct sunlight during this period, no other precautions are, in fact, usually observed.

During an investigation into the mechanism of oxidation of rubber and its bearing on accelerated aging tests, Morgan and Naunton[1] discovered that exposure to the diffused light of the laboratory could have a profound effect on the subsequent rate of oxidation of rubber. A diphenylguanidine-accelerated vulcanizate containing 1 per cent phenyl-β-naphthylamine was spread in crumbed form over a large sheet of glass and a similar sheet of glass supported on a wooden frame placed over it. The rubber was exposed in this way to ordinary daylight in the laboratory. After various times of exposure, part of the sample was removed and the rate of oxidation measured at 70° C in the dark. Representing the rate of oxidation of unexposed rubber as 1, the results obtained by these workers were as follows:

Exposed to light for 1 day	1.25
" " " " 4 days	1.96
" " " " 11 "	2.82
" " " " 22 "	3.45

It was found also that these enhanced rates of oxidation persisted during subsequent oxidizing in the dark, but that the effect decreased progressively with time, disappearing completely within 1 day at 70° C. It is suggested that the rate of oxidation is proportional to the concentration of peroxides formed, and that the effect of exposure to light is to increase the amount of these materials present and thereby accelerate subsequent oxidation. With a view to investigating this effect, Morgan and Naunton[1] carried out the following experiments on a transparent rubber sheet, 4 mm. thick (crepe 100, zinc oxide 2, sulfur 3.5, diphenylguanidine 0.5, vulcanized for 70 minutes at 141° C).

	Tensile strength (kg. per sq. mm.)	Elongation at break (percentage)
Unaged, stored in the dark	1.52	763
Unaged, exposed for 3 hours to winter sun	1.55	760
Stored in dark and then aged for 18 hours in bomb (70° C, 300 lbs. per sq. in. oxygen)	0.94	668
Light-exposed sample, aged simultaneously	0.16	350

A transparent sample was chosen for these tests, since it should show the maximum effect if, as is suggested, the effect varies (1) with the intensity of the light and (2) with the transparency of the compound.

* Reprinted from the *Journal of Rubber Research* of The Research Association of British Rubber Manufacturers, Vol. 12, No. 8, pages 87–90, August 1943.

To determine whether light would produce similar effects in lightly compounded rubbers and in rubbers heavily compounded with carbon black or zinc oxide, the following experiments have been carried out. The three mixings examined were:

	A	B	C
Smoked sheet	100	100	100
Stearic acid	1	3.1	2
Zinc oxide	5	7.6	65
Gas black	—	38.2	—
Diphenylguanidine	0.73	—	—
Mercaptobenzothiazole	—	0.78	—
Tetraethylthiuram disulfide	—	—	0.25
Sulfur	3	3.1	2

Stock A was vulcanized for 30 minutes at 153° C (60 lbs. per sq. in. steam pressure), stock B for 30 minutes at 148° C (50 lbs.), and stock C for 25 minutes at 126° C (20 lbs.) in the form of slabs 6 in. × 6 in. × 0.1 in. in moulds in a steam-heated platen-press. These times and temperatures were chosen as being approximately the optimum in each case.

FIRST EXPERIMENT

Mixing	Treatment	Aging	Tensile strength (lbs. per sq. in.)	Elongation at break (percentage)	Rigidity (lbs. per sq. in.) 300%	500%	700%
A	D	unaged	3860	780	200	610	2660
	LE		3740	730	250	775	3250
	LW		3355	710	250	775	3150
	D	bomb	2455	675	250	775	—
	LE	16 hr.	2125	635	175	750	—
	LW		1910	610	275	825	—
	D	bomb	295	280	—	—	—
	LE	30 hr.	—	—	—	—	—
	LW		335	260	—	—	—
B	D	unaged	4320	640	1175	2870	—
	LE		4400	615	1200	3000	—
	LW		4350	635	1225	3025	—
	D	bomb	2335	505	1225	2300	—
	LE	16 hr.	2135	455	1225	—	—
	LW		2350	495	1275	2350	—
	D	bomb	1060	320	925	—	—
	LE	30 hr.	—	—	—	—	—
	LW		1130	340	975	—	—
C	D	unaged	3985	750	300	1075	3125
	LE		4285	785	250	1025	3175
	LW		4350	775	325	1175	3225
	D	bomb	4090	745	375	1275	3425
	LE	16 hr.	3970	755	300	1200	3350
	LW		3980	745	400	1350	3600
	D	bomb	3795	755	350	1225	3175
	LE	30 hr.	—	—	—	—	—
	LW		3745	740	375	1275	3325

SECOND EXPERIMENT

Mixing	Treatment	Aging	Tensile strength (lbs. per sq. in.)	Elongation at break (percentage)	Rigidity (lbs. per sq. in.) 300%	500%	700%
A	D	unaged	4075	780	250	650	2900
	LE		3650	750	225	650	2650
	LW		3250	745	250	650	2775
	D	Geer	2725	635	275	1025	—
	LE	oven	2325	605	275	1025	—
	LW	5 days	2425	620	325	1075	—
	D	Geer	2850	640	275	1050	—
	LE	oven	2650	630	300	1050	—
	LW	7 days	2625	595	300	1100	—
B	D	unaged	4350	640	1275	2975	—
	LE		4275	615	1300	3050	—
	LW		4325	625	1250	3000	—
	D	Geer	3425	505	1650	3425	—
	LE	oven	3250	475	1800	—	—
	LW	7 days	3325	500	1700	3325	—
	D	Geer	2150	360	1575	—	—
	LE	oven	2150	370	1600	—	—
	LW	12 days	2100	380	1600	—	—
C	D	unaged	4475	790	275	1050	3300
	LE		4450	790	300	1050	3175
	LW		4275	770	325	1100	3400
	D	Geer	3450	680	375	1300	—
	LE	oven	3350	700	350	1200	—
	LW	7 days	3025	695	325	1150	—
	D	Geer	2750	675	325	1100	—
	LE	oven	2575	675	325	1050	—
	LW	12 days	2550	675	300	1000	—

D = kept in dark before aging.
LE = exposed to ESE light before aging.
LW = exposed to WNW light before aging.

Several vulcanized slabs of each mixing were then suspended for 48 hours in the light from a window facing east-south-east, and others in the light from a window facing west-north-west. The remainder were placed in the dark cupboard in which all the slabs had been stored since vulcanization.

After exposure, dumb-bell specimens[2] were cut from the slabs, their length being parallel to the mill grain.

Four specimens were cut from each slab, these being distributed among the various aging treatments so as to minimize as far as possible the effects of any slight inequalities in vulcanization between the different slabs.

In the first experiment, made in August 1938, bomb-aging only was carried out. As all the necessary specimens could not be put in the bomb at once, some of them had to be stored for a few days before aging; the intervals between exposure and the commencement of aging were 1 day for the specimens aged 16 hours, and 6 days for those aged 30 hours.

A second experiment, using exactly similar rubbers, was made in October 1938, two periods of Geer-oven aging at 70° C being given, namely, 5 and 7

days for mixing A, and 7 and 12 days for mixings B and C. The interval between exposure and the commencement of aging was only a few hours in this case. The bomb-aging tests were unavoidably delayed for about 6 weeks, and the results are therefore not quoted in full.

All bomb-aging was carried out at 70° C, and 300 lbs. per sq. in. oxygen pressure.

After aging, the test-pieces were conditioned for 24 hours in a thermostatically controlled chamber at 20° C, and finally tested on a Scott tensile-tester, with the lower grip moving at 20 inches per minute. Loads at 300, 500, and 700% elongations and the load and elongation at break were recorded. For each combination of exposure and aging conditions, four test-pieces from each mix were used. The results tabulated below are: for tensile strength, the mean of the two highest of the four; for elongation at break, the mean of the two corresponding elongations; for rigidity, the means of all four results in each case.

During the periods between vulcanizing and exposure to light, between exposure and aging, and between aging and testing, the specimens were kept as far as possible in the dark.

The effect of light on the tensile strength before aging is as follows:

% Change in Tensile Strength

	ESE light		WNW light	
	Expt. 1	Expt. 2	Expt. 1	Expt. 2
Mixing A	−3	−13	−10	−20
" B	2	1	−2	0
" C	8	9	−1	−4

Mixing A shows a definite decrease, whereas B and C appear on the whole not to be appreciably affected.

The tensile strengths after aging, expressed as percentage of that before aging, are shown below.

Mixing	Treatment	Expt. 1 (bomb)		Expt. 2 (Geer oven)	
		16 hours	30 hours	1st period	2nd period
A	D	64	8	67	70
	LE	57	—	64	73
	LW	57	10	74	81
B	D	54	25	79	49
	LE	49	—	76	50
	LW	54	26	77	49
C	D	102	95	77	61
	LE	93	—	75	58
	LW	92	86	71	60

In the bomb test, light has produced a noticeable effect. Excluding the 30-hour tests on A and B, where the figures are too low to give useful information, it will be seen that six out of the seven figures for light-exposed rubbers are lower than the corresponding ones for unexposed rubbers. Although none of the seven individual differences is significant in relation to the experimental error, their mean is significant, so that a real effect of light may safely be inferred.

In the bomb tests made as part of Experiment 2, where some six weeks elapsed between exposure and aging, the light effect was observed only with mixing A. After 16 hours' aging, this gave the following tensile strengths (percentage of unaged value): D 49, LE 34, LW 43. Samples aged for 12 hours, however, showed no such effect. This difference between Experiments 1 and 2 agrees with the observation of Morgan and Naunton[1] that the effect of exposure to light gradually disappears with the lapse of time.

In the Geer-oven tests the effect of previous exposure to light is not appreciable, only one isolated figure (mixing C, LW, first aging period) showing a marked difference from the corresponding unexposed figure. The absence of noticeable effect here may arise from the lower intensity of daylight in October compared with August. Alternatively, it may be due to the relatively long duration of the Geer test, since the rubber peroxide formed under the influence of light is fairly rapidly destroyed at 70° C,[1] and therefore would be active during only a small part of the test, whereas it would survive more or less throughout the bomb-aging period.

The effects of light observed in the present experiments are much smaller than those found by Morgan and Naunton[1]. This is probably because these investigators used a transparent rubber in their bomb-aging tests; they state that the effect of light exposure becomes smaller with decreasing transparency of the rubber until, with compounds containing carbon black, it cannot be detected at all. The present results agree with this insofar that the light effect appears to be less with mixing B, containing carbon black, than with the others.

CONCLUSIONS

The present experiments confirm the observations of Morgan and Naunton[1] by showing that exposure of vulcanized rubber to light may affect the results of oxygen-bomb aging tests made some days, or perhaps even weeks, afterwards. They show also that a few days' exposure to even diffused daylight may noticeably lower the tensile strength of unaged rubber.

With normal, *i.e.*, not transparent, rubbers the effect of light on subsequent aging is small, and indeed does not seem to be noticeable at all in relatively slow aging tests, such as that in the Geer oven.

Nevertheless, it is clearly advisable, as a precaution, to avoid unnecessary exposure to light of rubbers that are to be subjected to accelerated aging tests.

REFERENCES

[1] Morgan and Naunton, "Mechanism of oxidation of rubber and its bearing on accelerated aging tests", *Proc. Rubber Tech. Conf. London*, 1938, p. 599.
[2] Of the type shown in Figure 76B of Dawson and Porritt, "Rubber: Physical and Chemical Properties", Croydon, England, 1935.

DETERIORATION OF VULCANIZED RUBBER BY COPPER AND MANGANESE COMPOUNDS *

E. C. B. Bott and L. D. Gill

The deterioration of vulcanized rubber containing increasing percentages of copper and manganese compounds and the extent of the protection given to the stocks by a secondary naphthylamine have been investigated. Jones and Craig[1] showed that the addition of copper stearate made no difference to the type of aging of stocks containing various percentages of antioxidant when measured by decrease in tensile strength, and the results of Taylor and Jones[2] indicate that the decrease is proportional to the time of aging in the Geer oven.

Preliminary work.—Experiments were made on the base mix to determine its suitability and its optimum cure. The optimum cures of the base mix plus copper or manganese compounds after storage for six weeks in the dark at normal room temperature and of the base mix plus sym. di-β-naphthyl-*p*-phenylenediamine also were obtained.

The following compounds A, B, C and D were mixed on a laboratory mill having 12 × 6 in. rolls.

A

Base mix	Parts by weight
Smoked sheet	100
Blanc fixe	89
Zinc oxide	5
Sulfur	3
Stearic acid	2
Mercaptobenzothiazole	1
	200

B Base mix plus 0.021 per cent copper.
C " " " 0.034 per cent manganese.
D " " " 0.25 per cent symmetrical-di-β-naphthyl-*p*-phenylenediamine.

All are percentages by weight, based on the weight of rubber in the base mix.

Compounds A and D were stored for 24 hours, then vulcanized; B and C were vulcanized after storage for six weeks. All compounds were vulcanized at 134.5° C in the form of sheets approximately one-tenth inch thick, allowed to stand for 24 hours, dumb-bell test-pieces stamped out from the sheets, and the pieces pulled at room temperature on the Scott tensile testing machine at a rate of 20 inches per minute. The optimum cures of compounds A, B, C and D were obtained in 30 minutes with a tensile strength, based on the original cross-sectional area, of 3,280 ± 20 lbs. per sq. in.

The copper and the manganese were added in both cases in the form of their stearates because of the relative ease of dispersion of stearates compared to that of most other compounds of these metals.

* Reprinted from the *Transactions of the Institution of the Rubber Industry*, Vol. 19, No. 1, pages 53–58, June 1943.

The chemical analyses of the components are shown in Table 1.

TABLE 1

	Copper (percentage)	Manganese (percentage)
Base mix	0.000425	0.00015
Copper stearate	9.57	0.0003
Manganese stearate	0.00125	7.38

Blanc fixe was used as a filler in the base mix because of its freedom from compounds deleterious to aging, and because a mix containing filler gives more uniform results for tensile strength than a pure-gum stock.

These preliminary results showed that the addition of copper or manganese stearates or of the antioxidant to the base mix did not alter either the time of optimum cure or the tensile strength of the vulcanizate, sufficiently uniform results being obtained to enable further work to be done.

Deterioration of the vulcanized stocks.—Decrease in tensile strength was used as a measure of the deterioration of the samples of vulcanized rubber. Small percentages of copper and of manganese stearates were added separately to the base mix on the laboratory mill; the stocks were stored in the dark for periods of one day, two weeks and six weeks at room temperature and were then vulcanized for 30 minutes—the optimum cure—under the same conditions as the samples used for the preliminary work. Dumbbell test-pieces were stamped from the vulcanized sheets, and the pieces were aged for five days in the Geer oven at 82° C. The tensile strengths of these aged samples are given in Table 2.

TABLE 2

	Stored one day		Stored two weeks		Stored six weeks	
Copper (percentage)	Tensile strength (lbs. per sq. in.)	Deterioration (percentage)	Tensile strength (lbs. per sq. in.)	Deterioration (percentage)	Tensile strength (lbs. per sq. in.)	Deterioration (percentage)
0	2920	0	2854	0	2831	0
0.004	2720	6.8	2560	10.3	2485	12.2
0.008	2650	9.2	2555	10.5	2445	13.6
0.012	2460	15.8	2400	15.9	2335	17.5
0.014	2340	19.9	2230	21.9	2320	18.1
0.016	2290	21.6	2130	25.4	2085	26.4
0.018	2200	24.7	2040	28.5	1990	29.7
0.020	2020	30.8	2020	29.2	2010	29.0
0.040	2000	31.5	1940	32.0	1940	31.5
0.060	1800	38.4	1850	35.2	1855	34.5
Manganese (percentage)						
0	2820	0	2830	0	2740	0
0.005	2720	3.5	2650	6.4	2655	3.1
0.010	2630	6.7	2620	7.4	2555	6.8
0.015	2550	9.6	2590	8.5	2420	11.7
0.020	2480	12.1	2570	9.2	2400	12.4
0.025	2310	18.1	2285	19.3	2375	13.3
0.030	2290	18.8	2340	17.3	2295	16.2
0.035	2260	19.9	2180	23.0	2150	21.5
0.040	2140	24.1	2070	26.9	2040	25.5
0.050	1720	39.0	1860	34.3	1690	38.3
0.060	1540	45.4	1580	44.2	1570	42.7
0.080	1330	52.8	1320	53.4	1425	48.0
Base mix	2740	...	2800	...	2455	...

The percentages of metallic stearates were calculated to give definite percentages of the metal on the rubber, as shown in Table 2. The proportion of the deleterious metal already present in the base mix was taken into account in the calculations. Thus, copper 0.004 per cent on the rubber, or 0.002 per cent in the base mix, is made up of 0.000425 per ecnt copper already present on the base mix and 0.001575 per cent copper added as copper stearate, the amounts of manganese in the base mix and in the copper stearate being considered to have a negligible effect on the aged compound.

The deterioration (percentage) was obtained by plotting the tensile strength against the copper or manganese (percentage), finding the law for the best line or curve that could be drawn through the points, then calculating the tensile strength for zero concentration from the law; this tensile strength at zero concentration cannot be obtained directly from the result for the base mix because of the normal experimental error associated with the result for its tensile strength. It is necessary to obtain the most accurate result because the figures for deterioration depend on its value.

The ultimate elongations decreased somewhat when the percentages of the deleterious metals were increased, the maximum for the lower proportions being 620 per cent and the minimum for the higher proportions 570 per cent.

Further experiments showed that the deterioration produced by definite percentages of copper and manganese stearates in the same batch of base mix was proportional to the added copper and manganese, neither compound increasing the deterioration produced by the other one.

Protection by antioxidant.—The base mix plus 0.25 per cent of sym. di-β-naphthyl-*p*-phenylenediamine was mixed on the laboratory mill, small percentages of copper and of manganese stearates were mixed with it, the stocks were stored, vulcanized, aged, and tested for tensile strength under the same conditions stated in the preceding section on deterioration. The tensile strengths obtained are given in Table 3; the figures for zero concentrations of manganese were calculated as shown in the last section.

The ultimate elongations were 560 $\pm$ 20 per cent, and 580 $\pm$ 20 per cent for mixes containing copper and manganese stearates, respectively.

Summary of results.—The results given in Table 2 show that it is difficult to compare the relative deteriorations caused by copper and manganese stearates because the deteriorations follow different laws; the square root law for copper (see Figure 1) and the linear law for manganese (see Figure 2).

Approximate expressions for the deteriorations are: $D = 0.32\sqrt{[\mathrm{Cu}]}$ for copper and $D = 0.013$ [Mn] for manganese, where D is the deterioration (per cent) per day in the Geer oven at 82° C, and [Cu] and [Mn] are the amounts of copper and of manganese, respectively (parts per million on the rubber). Small percentages of copper produce about twice the deterioration caused by the same percentages of manganese.

The results in Table 3 show that good protection has been given by the antioxidant against the deleterious effect of copper stearate, the deterioration being little greater than the experimental error; therefore it cannot be calculated. Reasonable but slightly less protection was given against the bad effect of manganese stearate, where $D = 0.004$ [Mn] (see Figure 3).

Discussion of results.—Small proportions of copper have a proportionally greater deteriorating effect on a vulcanizate during aging than large proportions; thus, when batches were stored for one day, the first 0.004 per cent of copper produced an effect similar to an increase in copper from 0.04 to 0.06

TABLE 3

	Stored one day		Stored two weeks		Stored six weeks	
Copper (percentage)	Tensile strength (lbs. per sq. in.)	Deterioration (percentage)	Tensile strength (lbs. per sq. in.)	Deterioration (percentage)	Tensile strength (lbs. per sq. in.)	Deterioration (percentage)
0	...	...	...	...	...	...
0.004	2475	...	2645	...	2570	...
0.008	2545	...	2670	...	2620	...
0.012	2625	...	2710	...	2570	...
0.014	2540	...	2670	...	2600	...
0.016	2600	...	2540	...	2580	...
0.018	2530	...	2555	...	2490	...
0.020	2530	...	2455	...	2520	...
0.040	2400	...	2400	...	2515	...
0.060	2480	...	2370	...	2470	...
Manganese (percentage)						
0	2754	0	2793	0	2740	0
0.005	2705	1.8	2755	1.4	2710	1.1
0.010	2555	8.0	2760	1.2	2715	0.9
0.015	2630	4.5	2780	0.5	2580	5.8
0.020	2555	7.2	2690	3.7	2620	4.4
0.025	2485	9.8	2660	4.8	2460	10.2
0.030	2480	9.9	2655	4.9	2565	6.4
0.035	2485	9.8	2615	6.4	2550	6.9
0.040	2490	9.6	2615	6.4	2515	8.2
0.050	2455	10.9	2555	8.5	2520	8.0
0.060	2405	12.7	2450	12.3	2445	10.8
0.080	2400	12.9	2230	20.2	2270	17.1
Base mix plus antioxidant	2580	...	2700	...	2540	...

per cent. Small proportions of manganese produced about half the deterioration of small proportions of copper, and, unlike copper, equal increases in manganese concentration produced correspondingly equal increases in deterioration on aging.

Although successive periods of storage of uncured stocks containing manganese stearate made no change in the quality of the aged vulcanized rubber, small amounts of copper stearate, 0 to 0.018 per cent of copper on the rubber, gave cured samples of successively poorer aging properties after storage for one day, two and six weeks. Hence, mixes having a small copper content should be cured reasonably soon after preparation.

The results in Tables 2 and 3 have been arranged so that only deteriorations due directly to copper and manganese stearates are shown. It must be borne in mind that the tensile strength of the base mix after aging was not greater than 2,800 lbs. per sq. in., the result for the unaged base mix 3,280; this represents a decrease in tensile strength on aging of approximately 15 per cent.

The antioxidant, 0.25 per cent on the rubber, used in these experiments largely eliminated the bad effect of the copper stearate and prevented about 75 per cent of the bad effect of the manganese stearate, the effect of natural aging being presumed constant, a supposition which may be justified by comparing the calculated values of the tensile strengths of samples containing zero concentrations of the deleterious metals.

The results should be applied with discrimination, since different fillers, activating ingredients, accelerators and different compounds of copper and of manganese may modify the results. Although the work of this communica-

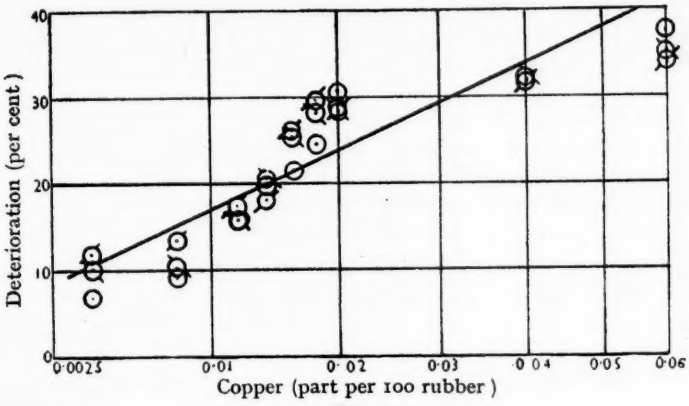

FIG. 1.

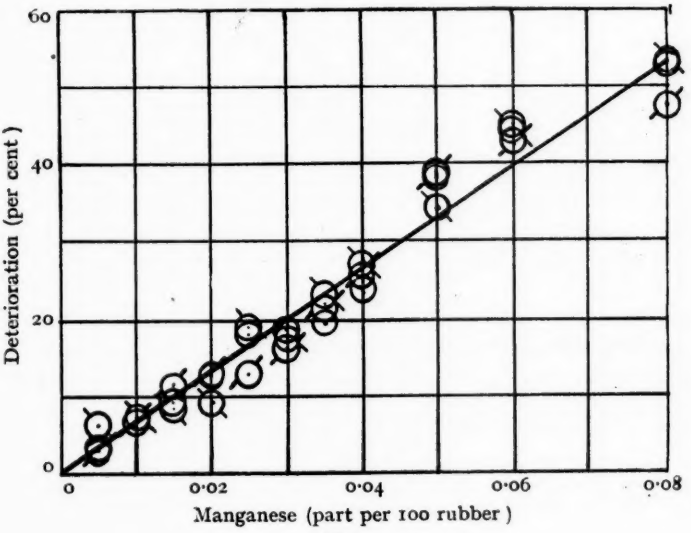

FIG. 2.

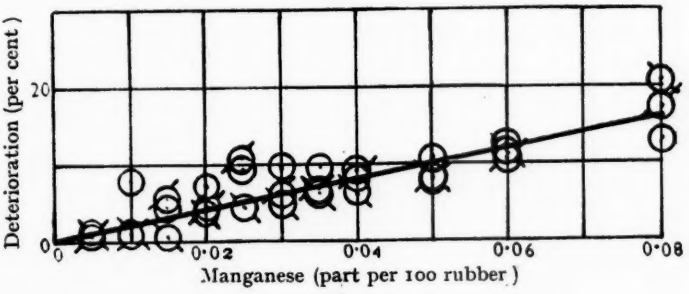

FIG. 3.

⊙ Stored one day. ⊙ Stored two weeks. ⊙ Stored six weeks.

tion was designed to yield technological results, the difference in the laws governing the deterioration caused by the copper and manganese salts appears to have some scientific application to the oxidation of vulcanized rubber containing them. Evidence exists that the oxidation of vulcanized rubber is somewhat proportional to the falling-off in mechanical properties in their measurable range, and these mechanical properties are usually used as a measure of the deterioration of the vulcanizate. Thus, it would appear that the stearates of copper and manganese may be changed to oxides, possibly by zinc oxide in the mix, which act as oxidation catalysts, respectively, in the following manner: $2\,CuO \xrightarrow{-O} Cu_2O \xrightarrow{+O} 2\,CuO$, and $MnO \xrightarrow{+O} MnO_2 \xrightarrow{-O} MnO$, oxygen being absorbed from the air and given up to the rubber in an active monatomic state, thus causing deterioration. In most systems, the amount of product is independent of the concentration of the catalyst, but in this system it has to be borne in mind that the catalyst, here the metallic oxide, and the reactant, vulcanized rubber, are immobile; therefore the catalyst can change the reactant only in its immediate vicinity. Thus, it is possible that the amount of the product of the reaction, the deteriorated rubber, is proportional to the concentration of the catalyst.

Conclusions.—The need for protection against the bad effects of copper and manganese compounds on vulcanized rubber is necessary and is of practical importance. In times of national emergency, such as the present, the protection becomes of more than usual importance. National economy in rubber is now the rule and, even when using ingredients of high quality, it is likely that the copper and manganese, expressed as percentages on the rubber, are greater than formerly, therefore the need for stressing the importance of the protection given by suitable antioxidants is quite evident.

ACKNOWLEDGMENT

The authors wish to thank the Directors of the Anchor Chemical Co., Ltd., Clayton, Manchester, 11, for permission to do this work in their laboratories and for permission to publish it.

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[2] Taylor and Jones, *Ind. Eng. Chem.* **20**, 132 (1928).

DETERMINATION OF TOTAL SULFUR IN RUBBER *

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With the recent increase in research on natural and synthetic rubber, there has arisen a need for a rapid method for the determination of total sulfur in rubber samples where only a semimicrosample can be spared for analysis.

The usual methods in which the rubber is oxidized by digestion with acid, followed in some cases by fusion to complete oxidation, and the sulfur is precipitated and weighed as barium sulfate, yield good results on semimicrosamples, but are time-consuming, because quantitative precipitation of the sulfate cannot be attained unless the solution is allowed to stand overnight before filtration. Several volumetric methods, most of which depend on the precipitation of sulfur as barium sulfate, have been described, but none is very satisfactory in the determination of small amounts of sulfur.

St. Lorant[1] has proposed a volumetric method for the determination of microsamples of sulfate, in which the sulfate is reduced to sulfide with hydriodic acid, and the hydrogen sulfide is distilled off and determined colorimetrically. The author has recently developed a modification of this method which has proved to be very satisfactory for the analysis of sulfur in small samples of rubber. The procedure consists essentially of oxidation of the rubber in the usual manner, reduction of the sulfate to sulfide, separation of the hydrogen sulfide by distillation, and titration of the latter iodometrically.

The new method is very rapid (20 to 25 minutes for the distillation and titration), and is not subject to the errors of adsorption, occlusion, and solubility encountered in the gravimetric barium sulfate method, or to difficulties in detection of the end-point encountered in some volumetric methods. It possesses the distinct advantage over some of the gravimetric methods that it is applicable to the analysis of rubber containing barium, lead, and calcium. The only serious objections to the method from the standpoint of general use are that hydriodic acid is expensive and that the applicability of the method is somewhat limited because of the fact that no more than about 5 mg. of sulfur can be handled conveniently. This means that the sample size must be small when analyzing rubber high in sulfur; and when small samples are used there is always the danger of error due to unequal distribution of sulfur in the sample.

APPARATUS

The apparatus is shown in Figure 1. It consists of a 125-cc. Erlenmeyer flask with standard taper 24/40 joint, a distillation head with capillary pressure regulator, and a 300-cc. Erlenmeyer flask with standard taper 24/40 joint. The capillary tubing is of 2 mm. inside diameter, and extends to within 2 to 4 mm. from the bottom of the 125-cc. flask.

REAGENTS

Nitric acid-zinc oxide-bromine mixture.—Dissolve 10 grams of zinc oxide in 100 cc. of nitric acid and saturate with bromine.

* Reprinted from *Industrial and Engineering Chemistry*, Analytical Edition, Vol. 15, No. 9, pages 602–604, September 15, 1943.

Acid mixture for distillation.—Place 160 cc. of hydriodic acid (specific gravity 1.70), 160 cc. of hydrochloric acid, and 45 cc. of hypophosphorous acid (50 per cent) in a 500-cc. Erlenmeyer flask. (If the hydriodic acid contains hypophosphorous acid as a preservative, use only 40 cc. of hypophosphorous acid). Add a few grains of silicon carbide, and boil vigorously without cover for 5 minutes. Cool in an ice-bath to room temperature. Keep stoppered

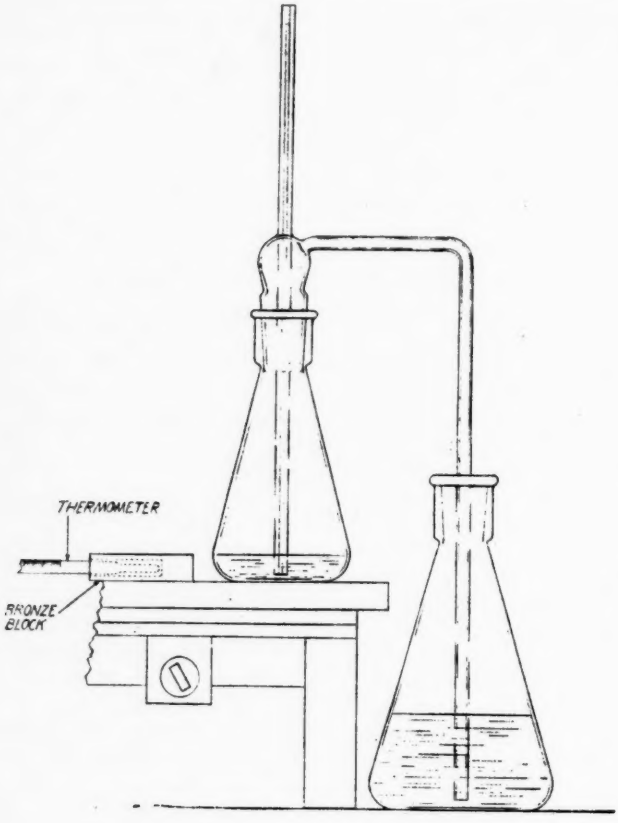

FIG. 1.

in a 500-cc. brown glass-stoppered bottle to avoid oxidation of the hydriodic acid.

Ammoniacal cadmium chloride solution.—Dissolve 10 grams of cadmium chloride dihydrate in water. Add 500 cc. of ammonium hydroxide and dilute to 5 liters.

Standard potassium iodate solution (0.01 *N*).—Recrystallize C. P. potassium iodate from water twice and dry at 180° C to constant weight. Weigh 0.7134 gram of the pure potassium iodate and dissolve in water. Add 2 grams of sodium hydroxide and then 10 grams of potassium iodide (free from potassium iodate). After complete solution of all salts, adjust to room temperature and dilute to 2 liters in a volumetric flask.

Standard sodium thiosulfate solution (0.01 *N*).—Dissolve about 5 grams of sodium thiosulfate pentahydrate in 2 liters of freshly boiled and cooled distilled water. Store in a clean Pyrex bottle. To standardize this solution, pipet 25 cc. of the standard potassium iodate solution into a 300-cc. Erlenmeyer flask. Add 200 cc. of water and 20 cc. of hydrochloric acid. Allow to stand 1 minute and then titrate with the thiosulfate solution. As the end point is approached add 10 cc. of 0.2 per cent starch solution and titrate carefully until the solution is colorless. The thiosulfate solution should be restandardized every 15 days.

Starch solution.—Add a cold aqueous suspension of 2 grams of soluble starch to 1 liter of boiling water. Cool to room temperature and store in a clean bottle.

PROCEDURE

Place 0.050 to 0.100 gram of the rubber sample, which has been either crumbed or cut into as small pieces as possible, in a 125-cc. Erlenmeyer flask with ground-glass joint. (The method as written is applicable to the analysis of semimicrosamples of rubber. If an analysis of larger samples is desired, appropriate increases in the amounts of reagents must be made. It is best, however, to limit the amount of sulfur in the sample to 5 mg. or less.)

(When a highly saturated material such as Butyl rubber is to be analyzed, it is desirable to limit the sample size to 0.05 to 0.10 gram to decrease the time of oxidation and danger of explosion with perchloric acid. In general, oxidation of difficultly oxidizable material is more rapid and convenient with the perchloric acid method than with the A. S. T. M. method.)

Proceed by either of the following methods:

A. S. T. M. method.—Add 4 cc. of nitric acid-zinc oxide-bromine mixture. Cover and heat on a steam bath or low-temperature hot plate to decompose the sample. When rapid solution ceases, add 3 cc. of fuming nitric acid. Cover and, while swirling the flask to prevent ignition of the sample, heat on a hot plate with surface temperature maintained at 180° to 200° C. When danger of ignition is past, allow the solution to boil gently until most of the organic matter is destroyed and the acid is all but expelled. With difficultly oxidizable samples, such as Buna-S and Butyl rubber, it may be necessary to add more fuming nitric acid and take down to near dryness 2 or 3 times before enough of the sample has been oxidized to make it safe to continue. Finally, remove the cover and bake over a Tirrill flame until the zinc nitrate is converted to zinc oxide and most of the brown fumes are expelled. Return the flask to the hot plate to cool and to allow the remaining fumes to be expelled. Cool to 30° C. Wash down the sides of the flask with 5 cc. of hydrochloric acid, and boil without cover to expel about half of the acid. It is essential that all nitrates be expelled to avoid interference in the titration described below. Cool to room temperature and reserve the solution for the distillation.

Perchloric acid method.—Proceed as directed in the A. S. T. M. method. When most of the readily oxidizable organic matter has been oxidized, and all but 1 or 2 cc. of the acid has been expelled, add 5 cc. perchloric acid (60 per cent). Cover and boil gently at a hot-plate temperature of 180° to 200° C, until white perchloric acid fumes appear. During this boiling it is essential that the flask be completely covered with a watch glass. With difficultly oxidizable material such as Butyl rubber, considerable amounts of organic material may remain after expulsion of the nitric acid. If this occurs, oxida-

tion with perchloric acid should be allowed to proceed only to the point where the sample begins to char. At this point add more fuming nitric acid, and repeat the evaporation. Repeat if necessary. Finally, when most of the organic matter is destroyed, the sample can safely be heated until fumes of perchloric acid appear without danger of ignition or explosion. Fume vigorously on a flame without cover to expel all but about 2 cc. of the acid. Cool to room temperature and reserve for the distillation.

After oxidation of the sample, add about 5 grains of silicon carbide (12-mesh grains that have been boiled in hydrochloric acid) to prevent bumping, and 35 cc. of the acid mixture, and immediately cap with the distillation head. Place on a hot plate with surface temperature of 375° to 400° C, and boil for 5 minutes, catching the distillate in 150 cc. of ammoniacal cadmium chloride solution in a 300-cc. Erlenmeyer flask with ground-glass joint. The boiling should be timed from the moment fumes of ammonium chloride are first seen in the 300-cc. flask.

Remove the small flask from the plate and detach the distillation head. (If difficulty is encountered in removing the head, cool the joint and then run hot water on it.) Cool the distillate rapidly in an ice-bath to 10° C. (In the analysis of samples containing over about 5 mg. of sulfur, add an excess of potassium iodate to a 125-cc. flask containing 20 cc. of hydrochloric acid and 20 cc. of water. Pour this solution in one stroke into the flask containing the sample. Stopper immediately and shake to oxidize all the sulfide in the flask. Wash the remains of the iodine into the large flask and back-titrate with thiosulfate as directed.)

Add 20 cc. of hydrochloric acid and swirl once to mix thoroughly. Titrate immediately and rapidly with potassium iodate solution, using a rapidly flowing buret—(*i.e.*, a 50-cc. buret which will empty by gravity in 60 to 70 seconds)—until an excess of about 1 or 2 cc. has been added, as indicated by the yellow color. Cap immediately with a ground-glass stopper, and shake vigorously to entrap any hydrogen sulfide in the atmosphere in the flask. Allow the potassium iodate buret to stand 1 minute after the titration before reading it. Add 10 cc. of starch solution and titrate with standard sodium thiosulfate solution (0.01 *N*). Carry a blank through the whole procedure. The blank should not be greater than 0.1 cc. of potassium iodate solution (0.01 *N*):

$$\frac{[(\text{Ml. of } KIO_3 - \text{cc. of } Na_2S_2O_3 \times KIO_3 \text{ factor}) - \text{blank}] \times 0.01603}{\text{Sample weight in grams}} = \text{per cent sulfur.}$$

DISCUSSION

The proposed volumetric method for the determination of sulfate yields satisfactory results when the amount of sulfur to be determined is less than about 10 mg., although slightly low values are obtained when the amount of sulfur present exceeds about 1 mg. (see Table I). With quantities greater than about 5 mg., special precautions must be taken to avoid loss of hydrogen sulfide during the titration.

Low results are obtained if the hydrogen sulfide is allowed to escape during the distillation or titration, if the temperature of distillation is too low, if the concentration of hydriodic acid is too low, and if nitrates in quantities greater than traces are present at the distillation. High results may be obtained

unless a blank correction for the reagents is made. Because of the danger of exceptionally heavy contamination of the hypophosphorous acid with sulfur compounds, it is necessary to resort to a preliminary distillation of the acid mixture to reduce the blank to a reasonable figure.

In preliminary work, the usual distillation apparatus for the evolution method for sulfur in steel was used. This proved unsatisfactory because the variation in the diameter of the Neoprene rubber stoppers and the neck of the Erlenmeyer flasks was so great that the distance between the bottom of the

TABLE I

DETERMINATION OF SULFUR IN POTASSIUM SULFATE BY THE PROPOSED VOLUMETRIC METHOD

No.	Sulfur present (mg.)	Sulfur found (mg.)	Error (mg.)
1	0.06	0.07	+0.01
2	0.13	0.13	±0.00
3[a]	0.13	0.13	±0.00
4	0.25	0.25	±0.00
5	0.62	0.61	−0.01
6[b]	0.62	0.62	±0.00
7	1.25	1.24	−0.01
8[a]	1.25	1.22	−0.03
9[b]	1.25	1.23	−0.02
10[c]	1.25	1.22	−0.03
11[d]	1.25	1.22	−0.03
12[e]	1.09	1.08	−0.01
13	3.12	3.10	−0.02
14[b]	3.12	3.09	−0.03
15	6.23	6.16	−0.07
16[b]	6.23	6.20	−0.03

[a] Titrated with KIO_3 using CCl_4 as indicator.
[b] No $HClO_4$ present in acid mixture.
[c] 0.2 gram of $BaCl_2 \cdot 2H_2O$ present.
[d] 0.05 gram of $PbCl_2$ present.
[e] Different K_2SO_4 solution used.

flask and the end of the capillary pressure regulator could not be conveniently controlled. In the apparatus finally chosen, the rubber stopper was replaced by a standard taper ground-glass joint.

When hydrogen sulfide is titrated directly with standard iodine, using starch as indicator, the end-point is very poor, owing to the appearance in the solution of a permanent reddish color, which obscures the blue of the end point. The color is probably caused by the adsorption of some compound of iodine and sulfur on the starch molecule. As evidence of this, it is noted that very little free sulfur appears during the titration of those solutions which contain starch. Experiments indicated that the red color is more pronounced the colder the solution and the greater the salt concentration, especially if the salt is an iodide. It was found that, in the titration of hydrogen sulfide in solutions containing but small quantities of salts, the red color could be almost completely eliminated by adding about 0.5 mg. of mercuric iodide or mercuric chloride to the solution or by titrating at 35° to 40° C. Unfortunately, the addition of mercury caused the results to be slightly low, probably because of the conversion of part or all of the mercury to sulfide. Because of this, and the fact that the use of mercury salts is not very effective in the presence of appreciable quantities of salts, the problem was not considered further.

The best method for titrating hydrogen sulfide is that in which an excess of iodine is added, followed by back-titration with thiosulfate, using starch as indicator. This method has the advantage that the end-point is good and the danger of loss of hydrogen sulfide can be greatly reduced by rapid over-titration with iodine using a fast flowing buret.

It will be seen in the procedure that no extra iodide is added to the solution previous to titration, as is sometimes done in direct titrations of sulfide with iodine. This addition is unnecessary and, in fact, is purposely omitted in the method because a considerable amount of hydriodic acid comes over with the hydrogen sulfide, and any further addition of iodide is detrimental to the starch-iodine end-point.

The two gravimetric methods most often used for the determination of sulfur in rubber stocks which are free from barium and large amounts of lead and calcium are those of Wolesensky[2] (hereinafter called the perchloric acid method), and Kratz, Flower, and Coolidge[3] (hereinafter called the A. S. T. M. method). In the analysis of representative samples of natural and synthetic rubber stocks, these two methods give results which are in good agreement. In like manner it was found (see Table II) that results obtained by the pro-

TABLE II

DETERMINATION OF TOTAL SULFUR IN NATURAL AND SYNTHETIC RUBBER USING PROPOSED VOLUMETRIC METHOD

No.	Rubber sample	Percentage sulfur found: Gravimetric $HClO_4$ method	New volumetric method: $HClO_4$ oxidation	New volumetric method: A. S. T. M. oxidation
1	Buna-S gum stock	0.19	0.19	...
2		0.19	0.20	...
3	Gum rubber 1	0.63	0.62	0.63
4		0.63	0.62	0.62
5	Gum rubber 2	1.88	1.87	1.85
6		1.88	1.86	1.87
7	Gum rubber 3	3.55	3.52	3.50
8		3.55	3.48	3.50
9		3.55	3.47	3.48

posed volumetric method and the perchloric acid method check very well, although, as would be expected from the data in Table I, the volumetric method gives somewhat lower results.

In agreement with Wolesensky, it was found that great care must be taken to prevent loss of sulfur during digestion of rubber samples with nitric and perchloric acids. The loss is negligible if the sample is digested slowly in a long-necked Kjeldahl flask. When a small Erlenmeyer flask is used, however, the loss may amount to 1 or 2 per cent (when the new volumetric method is used for the final determination), unless the digestion is slow and the flask is kept completely covered with a watch-glass until all organic matter is expelled. In the procedure an attempt has been made to minimize this loss by delaying the addition of the perchloric acid until most of the readily oxidizable material has been oxidized. After oxidation of the organic material, the sample can be taken to copious fumes of perchloric acid without loss of sulfur, providing an excess of zinc is present. This suggests that the sulfur, which is lost during the digestion of the organic matter, has not been oxidized to sulfate. No loss of sulfur is encountered when the A. S. T. M. method is used.

EXPERIMENTAL

A standard solution of potassium sulfate was prepared by dissolving 0.6780 gram of the pure dry salt in water and diluting to 1 liter in a volumetric flask. Aliquot portions of the solution were evaporated to dryness in 125-cc. Erlenmeyer flasks. The samples were then analyzed for sulfur as directed in the procedure, except that an acid mixture of the following proportions was used: 100 cc. of hydriodic acid (specific gravity 1.70), 100 cc. of hydrochloric acid, 25 cc. of hypophosphorous acid (50 per cent), and 25 cc. of perchloric acid (60 per cent). The results are shown in Table I.

Four representative types of rubber stocks (containing no barium, lead, or calcium) were analyzed for sulfur, as directed in the procedure. Results were obtained using both the A. S. T. M. and the perchloric acid methods of oxidation. The samples were also analyzed by the gravimetric perchloric acid method. The results are given in Table II.

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DETERMINATION OF MERCURY IN RUBBER *

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It has recently been necessary to determine small amounts of mercury (0.1 to 5.0 per cent) in natural and synthetic rubber compounds containing iodine. A survey of the literature showed that the method most often used for the determination of mercury in organic compounds containing iodine involves complete oxidation of the carbonaceous material by digestion with acid, followed by separation of the mercury from the iodine by reduction of the former to the metallic state and filtration[1]. In searching for a more convenient method of separation, it was found that this can be accomplished very simply by boiling with nitric acid under controlled conditions. Free iodine is expelled with but little loss of mercury, which can then be titrated with thiocyanate. The new method has been applied successfully to the determination of mercury in rubber samples containing iodine (see Table III).

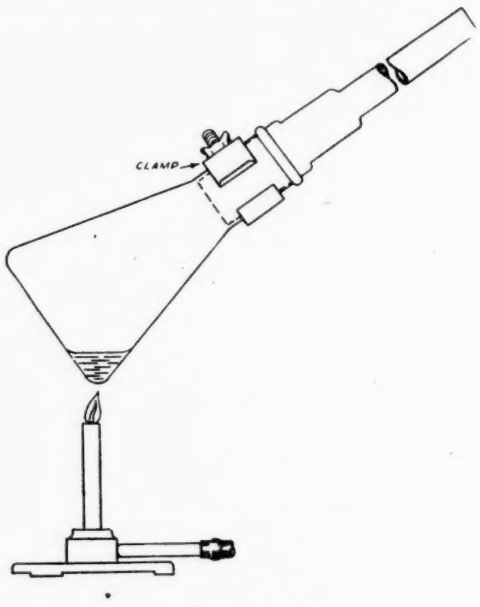

FIG. 1.—Digestion apparatus.

APPARATUS

The apparatus is shown in Figure 1. It consists of a 125-cc. Erlenmeyer flask with standard taper 24/40 joint connected to an air condenser 80 cm. long and 1 cm. inside diameter.

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REAGENTS

Standard mercury nitrate solution.—Dissolve approximately 0.5 gram of pure mercury in 10 cc. of nitric acid in a 1-liter volumetric flask. Add 25 cc. of water and cool to room temperature. Draw off most of the brown fumes and dilute to the mark with water.

Standard ammonium thiocyanate solution (approximately 0.01 *N*).—Dissolve approximately 1.8 grams of ammonium thiocyanate in water and dilute to 2 liters. To standardize this solution, pipet 50 cc. of the standard mercury solution into a 125-cc. flask. Add 3 cc. of sulfuric acid, 5 cc. of nitric acid, and 0.2 gram of potassium sulfate. Color with permanganate and titrate as directed in the procedure.

Ferric alum indicator.—Dissolve 30 grams of ferric alum [$FeNH_4(SO_4)_2 \cdot 12H_2O$] in 95 cc. of water and add 5 cc. of colorless nitric acid.

PROCEDURE

Weigh 20 to 100 mg. of the subdivided rubber sample and place in a dry 125-cc. Erlenmeyer flask with standard taper joint, taking care not to allow particles of the sample to cling to the walls or neck of the flask. Add about 0.3 gram of potassium persulfate ($K_2S_2O_8$) and tap the flask to collect the rubber particles to one side of the bottom of the flask. Add 2 cc. of fuming sulfuric acid and cap tightly with a dry 80-cm. air condenser. (If the rubber sample weighs more than 50 mg., it is best to use 0.5 gram of potassium persulfate and 3 cc. of fuming sulfuric acid.) Clamp the neck of the flask to a ring stand and tilt the flask so that the acid covers the rubber sample.

Place in a hood, and play a small flame from a Tirrill semimicroburner on the flask below the acid mixture. Heat gently to decompose the sample, taking great care to prevent loss of iodides of mercury. It is necessary to keep the flame low during the initial oxidation, so that evolution of white fumes from the tip of the condenser is not too vigorous. As the oxidation proceeds, the flame can be increased until, in the later stages, the acid boils and bumps. Under no circumstances must the top half of the air condenser be allowed to get even warm. When destruction of the organic matter is complete, remove the flame, and allow the flask to cool.

Wash down the walls of the condenser with 15 to 20 cc. of nitric acid (1 to 1). Detach the air condenser and wash the joint with water from a wash bottle. If the sample contains less than 5 mg. of mercury, set the condenser aside. Cover the flask with a small watch-glass, heat to gentle boiling on a hot plate (do not use a flame), and boil until all the iodine is expelled, *i.e.*, until the solution and vapor are entirely free of color due to iodine, and no insoluble iodides of mercury can be seen in the solution. After iodine is expelled, evaporate (rapidly if desired) to about 10 cc. (In case traces of organic matter remain in the solution, evaporate until white fumes begin to be evolved and then add 5 cc. of nitric acid, 1 to 1.) Cool and reserve.

If the sample contains more than 5 mg. of mercury, replace the air condenser after washing the joint, and expel the iodine as directed above, omitting the use of a watch-glass. If some iodine collects in the condenser joint during boiling, cool the solution somewhat, break the joint, and allow the iodine to escape. Replace the condenser and continue boiling.

Wash down the sides of the flask (or flask and condenser) with water, and remove the condenser if used. Dilute to 30 to 50 cc. with water and cool to

room temperature. Add potassium permanganate (2 per cent solution) dropwise until a color is obtained which persists. Dispel the color with a drop or two of 3 per cent hydrogen peroxide. Add 0.5 to 1.0 cc. of ferric alum indicator solution, and titrate carefully with 0.01 *N* ammonium thiocyanate solution until the first permanent brownish red color is obtained in the solution. Provide for blank correction:

$$\frac{\text{cc. of } NH_4CNS \times \text{Hg factor} \times 100}{\text{Sample weight in grams}} = \text{per cent mercury.}$$

DISCUSSION

Rubber samples containing mercury and iodine cannot be completely oxidized by treatment with sulfuric acid and 30 per cent hydrogen peroxide or by other mild methods of oxidation. After testing various methods, it was found that the oxidation is best accomplished by the Kjeldahl method of Sloviter, McNabb, and Wagner[2]. In view of the volatility of iodides of mercury and the ease with which they are mechanically carried out of the condenser by the escaping fumes of sulfur dioxide, the rate of digestion must necessarily be slow. Because of this, and in view of the fact that rubber samples containing mercury and iodine are difficult to oxidize, it is best to limit the sample size to 100 mg. or less. Oxidation of certain synthetic rubber samples, such as Buna-S and Butyl rubber, may take several hours, even when the sample size is small. Attempts to decrease the time of oxidation by the use of selenium as a catalyst or by employing the Parr bomb were not successful, as low results were obtained.

With the conditions recommended in the procedure, some loss of mercury occurs during the expulsion of the iodine if the amount of mercury present is greater than about 5 mg. The loss may amount to as much as 2 or 3 per cent in some cases, but for many purposes this accuracy is satisfactory (see Tables I and II).

In preliminary work, 30 per cent hydrogen peroxide was used to convert the iodide to free iodine. Very low results were obtained, however, when samples containing large amounts of mercury and iodine were analyzed. This

TABLE I

DETERMINATION OF MERCURY BY THE VOLHARD METHOD
(After expulsion of iodine with nitric acid)

No.	HNO_3 (1 : 1) added (cc.)	Hg added (mg.)	Hg found (mg.)	Error (mg.)	Error (%)
1[a]	10	1.1	1.1	0.0	...
2	10	3.7	3.7	0.0	...
3	10	5.1	5.1	0.0	...
4[a]	20	5.0	5.1	+0.1	2.0
5	20	5.6	5.6	0.0	...
6	20	5.7	5.6	−0.1	1.8
7	20	10.1	9.8	−0.3	3.0
8	20	12.8	12.4	−0.4	3.1
9	50	11.7	11.3	−0.4	3.4
10	50	19.2	18.8	−0.4	2.1
11	50	70.0	69.0	−1.0	1.4
12	25	100.0	98.0	−2.0	2.0
13	50	93.7	91.0	−2.7	2.9

[a] 200 mg. of K_2SO_4 added with HgI_2.

TABLE II

DETERMINATION OF MERCURY BY THE VOLHARD METHOD
(After expulsion of iodine with nitric acid, air condenser used)

No.	Hg added (mg.)	Hg found (mg.)	Error (mg.)	Error (%)
1	0.7	0.7	0.0	...
2	2.7	2.7	0.0	...
3	9.2	9.1	−0.1	1.1
4	13.4	13.3	−0.1	0.7
5	31.6	30.9	−0.7	2.2
6	53.8	52.7	−1.1	2.0
7	118.2	116.6	−1.6	1.4

probably resulted from the comparatively low acidity and the decrease in oxidizing strength of the solution as it is boiled. Nitric acid was found to be superior to hydrogen peroxide. The optimum concentration of the acid appeared to be about 1 to 1.

According to Hillebrand and Lundell[3], loss of mercury by volatilization as chloride is controlled, to a large extent, by the shape of the vessel and concentration of the mercury in the solution. The same appears to be true in the present case. Thus, Tables I and II indicate that the loss of mercury increases with an increase in the amount of mercury present, and is reduced appreciably by the use of a long reflux tube.

While the actual loss of mercury increases with an increase in the amount of mercury present, the percentage loss first increases and then tends to decrease. The use of the air condenser appears to shift upward the concentration at which the maximum per cent error is obtained. Finally, in the expulsion of iodine, the more vigorous the boiling, the greater the tendency for loss of mercury.

In the determination of mercury in readily oxidizable organic materials, where nitric acid can be used as the oxidant, it may be possible to oxidize the sample and expel the iodine simultaneously. It is also probable that mercury can be separated from chloride or bromide by boiling with nitric acid.

During the development of the proposed method, an attempt was made to determine the mercury in the digestion mixture directly by the Rupp method[4] without removing the iodine. Preliminary experiments in which known amounts of pure mercuric iodide were analyzed for mercury by the Rupp method showed that low results were obtained when the amount of mercury exceeded about 2 mg. In agreement with Fitzgibbon[5], it was found that the addition of gelatin was beneficial. By adding 2 cc. of 1 per cent gelatin solution to the sample before reduction with formaldehyde, correct results could be obtained with quantities of mercury up to 5 mg. With larger amounts, low results were obtained, and a black precipitate which is insoluble in standard iodine solution remained in the bottom of the flask.

When mixtures of rubber and weighed quantities of mercuric iodide (< 5 mg. of mercury) were carried through the complete procedure, very low results were obtained. The cause was finally traced to the presence of free iodine in the solution previous to reduction of the mercury with formaldehyde. This iodine was produced in the following manner. After complete oxidation of the rubber the condenser was washed down with 10 cc. of 5 per cent potassium iodide solution; bromine water was added dropwise to oxidize the mercury and sulfur dioxide; when a slight permanent precipitation of iodine occurred

the flask was stoppered and shaken to oxidize all the sulfur dioxide; and after 5 minutes the analysis for mercury by the Rupp method was made.

Theoretically, free iodine should cause no trouble in the reduction of mercury with formaldehyde, since the hypoiodite is reduced to iodide. Actually, however, when iodine is present the mercury is precipitated in a form that does not dissolve completely in standard iodine solution. Black specks of undissolved material and cloudy solutions are encountered, and the results are very low.

Attempts to improve the results by titration of the free iodine in acid solution with sulfite or thiosulfate failed, as did also reduction of the iodine with hydrogen peroxide in alkaline solution. It was therefore concluded that the Rupp method could not be used for direct analysis of the mercury in the digestion mixtures. The only satisfactory procedure found was that in which the iodine was expelled by boiling with nitric acid, followed by complete expulsion of all nitrates, and finally, addition of potassium iodide, and analysis

TABLE III

DETERMINATION OF MERCURY IN RUBBER-MERCURIC IODIDE MIXTURES

No.	Hg added (mg.)	Hg found (mg.)	Error (mg.)
1	0.1	0.1	0.0
2	0.5	0.5	0.0
3	0.7	0.7	0.0
4	1.9	1.9	0.0
5[a]	3.0	3.0	0.0
6[b]	4.2	4.2	0.0
7[c]	4.6	4.6	0.0
8	6.2	6.1	−0.1
9[d]	6.4	6.2	−0.2
10[e]	0.5	0.5	0.0
11[e]	2.5	2.5	0.0
12[e]	5.6	5.6	0.0
13[e]	5.8	5.7	−0.1

[a] 25 mg. of KI added with HgI_2.
[b] 100 mg. of rubber, 0.5 gram of $K_2S_2O_8$, and 3 cc. of fuming H_2SO_4 used.
[c] 0.5 gram of $K_2S_2O_8$ and 3 cc. of fuming H_2SO_4 used.
[d] 50 mg. of KI added with HgI_2.
[e] Mercury determined by Rupp method.

by the Rupp method in the usual way employing gelatin. This method has been shown to be satisfactory for small amounts of mercury (see Table III), but because of its limited applicability and its complexity it does not compare with the Volhard method.

EXPERIMENTAL

Weighed quantities of pure mercuric iodide together with 3 cc. of sulfuric acid and various quantities of nitric acid (1 to 1) were placed in 125-cc. Erlenmeyer flasks. The iodine was then expelled and the mercury determined by the Volhard method as directed in the procedure, without use of the air condenser. Results are recorded in Table I.

The experiment was repeated, using an 80-cm. air condenser. The mercuric iodide was treated with 3 cc. of sulfuric acid, 15 cc. of nitric acid (1 to 1), and 0.2 gram of potassium sulfate. The results are recorded in Table II.

Weighed quantities of pure mercuric iodide and 20 to 30 mg. of a mercury-free gum rubber stock were placed in 125-cc. Erlenmeyer flasks. The samples

were then treated as directed in the procedure, using 0.3 gram of potassium persulfate and 2 cc. of fuming sulfuric acid. No air condenser was employed in the expulsion of the iodine. The results are recorded in Table III.

SUMMARY

A very simple method has been developed for the separation of iodine from mixtures of mercury and iodine previous to determination of the mercury by the Volhard method. The method has been applied successfully to the determination of small amounts of mercury in rubber samples containing iodine. The Rupp method has been investigated.

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WILD RUBBER OF TROPICAL AFRICA *

GEO. MARTIN

By common usage the term rubber has come to denote the product of *Hevea brasiliensis*, which is outstandingly the most economical producer of rubber hydrocarbon known to mankind, and yields a product which, for general utility, has not yet been surpassed. There are, however, hundreds of other plants which yield rubber and before the advantages of *Hevea* became firmly established, many of them were the subject of preliminary investigation, but the information available, judged by present standards, is incomplete, out of date, and would not enable a modern manufacturer to convert wild rubber into articles of assured quality. This is not because wild rubber hydrocarbon is necessarily inferior or different from that of *Hevea*, but because of the well-known fact that the chemical behavior of rubber, including capacity for vulcanization and resistance to oxidation, is modified in considerable detail by small quantities of some nonrubber substances, many of which are natural components of plants. These components are not always the same for plants of the same species, and are known to be different in plants of different species.

Rubber-bearing plants are found in most countries, but outside the tropics, few of them yield enough rubber to make their cultivation worth while, even in these difficult times. The most prolific source of wild rubber is tropical and subtropical Africa, where there are known to be hundreds of different species of plants which yield appreciable quantities of moderately pure rubber, in addition to many plants which yield resinous latices, some of which are known to contain rubber and others of which, although previously not known to contain rubber, are now found to contain amounts which under present conditions may be regarded as appreciable.

It is convenient to divide the rubbery material produced in Africa into three main groups: (1) *rubber*, which, when clean and dry, contains 75 per cent and over of rubber hydrocarbon; (2) *resinous rubber*, containing between 40 and 75 per cent of rubber hydrocarbon; and (3) *rubbery resin*, which contains from 10 to 40 per cent of rubber hydrocarbon. This classification is based on the value of the material to the manufacturer. For example, the material in group (1) could be used satisfactorily for practically all purposes for which *Hevea* is used as long as the rubber present is not degraded. The material in group (2) could obviously only be used in small quantities or for special purposes because of the physical effect of the resin. The material in group (3) is still more difficult to use, and may require purification if received in sufficient quantity.

Plants which yield rubber in the first group are the only ones which are normally of interest and they are, therefore, the most familiar. The best known is the African rubber tree, *Funtumia elastica*, which is a tall forest tree growing throughout the moist regions of tropical Africa. It may not be as important, however, as the many species of vines and climbing shrubs which grow over a still wider area and, owing to their reproductive character, have had a better chance of recovering from the ruthless exploitation which occurred at the beginning of the present century.

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There are other rubber-yielding trees in Africa, but they have been imported, and are not so important as the indigenous wild rubber. In addition to old *Hevea* plantations in various parts of tropical Africa and *Hevea* rubber in Liberia, there are plantations of Ceara rubber (*Manihot glaziovii*), and experiments have been made in planting the India rubber tree (*Ficus elastica*) and *Castilloa*. All these yield in importance, however, to *Funtumia elastica* and the rubber vines of which the *Landolphia* species are the most prominent.

Funtumia elastica.—This is a tree growing throughout the moist hot regions of tropical Africa, mostly in dense forest, which, in some regions, contains a high proportion of the rubber tree. Under these conditions it grows with a straight trunk, which does not branch except at great height. The tree is usually tapped on the herring bone system, frequently to a height of 60 feet, the tapper climbing the tree for the purpose by means of slings. The vertical channel is made as the tapper ascends and lateral channel at from 6 to 12 inches apart as he descends. The tree yields about 0.25 pound of dry rubber per tapping, and should not be tapped more than twice a year. Destructive methods of tapping, which in some cases involved the felling of small trees, were prevalent for some time and wide areas are stated to have been depleted of this tree. Since then new growth has had time to become established.

Almost identical with *Funtumia elastica* is *Funtumia africana*, which is widely distributed in West Africa in the same situations as *F. elastica*. To the natives of Africa the former is known as the male and the latter as the female, and it requires a certain amount of experience to distinguish between them. Both yield latex on tapping, but whereas the latex of *elastica* contains rubber, that of *africana* contains only a sticky resin. In certain parts of Uganda is found a third species of *Funtumia*, *viz.*, *F. latifolia*, which yields a latex containing resin and some rubber. One of the tests for determining the species of a *Funtumia* tree is to roll the latex between finger and thumb to see whether it contains rubber. The difference in the composition of the latices of these trees is of considerable scientific interest in connection with the natural synthesis of rubber. Unfortunately, it is also of practical importance because the weight of crude rubber produced can be increased easily by diluting rubber latex with resin latex. The chief safeguard against this is the experience of the local purchaser and a price grading scheme which will penalize adulteration. Such a scheme is now in operation, and none of the consignments so far examined appear to have been adulterated with resinous latex.

Vines.—The rubber vines are thick, strong, woody climbers which attain a great size and are widely distributed in Africa, mostly in the forests as far north as Abyssinia and French West Africa, and nearly as far south as South Africa. The principal genera are *Landolphia*, *Clitandra* and *Carpodinus*. There are at least 20 species of *Landolphia* vines, of which the most important are *heudolotii* and *owariensis* in West Africa and *kirkii* and *ugandensis* in East Africa. The distribution of these species is, of course, not confined to these regions. The *Clitandra* and *Carpodinus* species are not so numerous as those of *Landolphia*, but are of importance.

In some districts where these plants are growing in open ground with no large trees for support, they develop into bushes or shrubs which throw up fresh shoots annually. The bulk of the rubber exported from Angolia is root rubber obtained from underground stems which are thrown out by some of the shrubs. These stems are a few inches below the surface of the soil and ramify in all directions. An underground stem of 60 yards without a break has been

recorded by Christy ("African Rubber Industry", 1911, p. 29). The stems rise above the ground every 30 or 50 feet and develop small tufts of foliage. *Landolphia thollonii* and *Carpodinus lanceolata* are the principal sources of this type of rubber.

Most of the rubber-yielding vines are slow growers, but *Cryptostegia grandiflora* is of particular interest under present circumstances because of its rapid growth. It is a native of India and Madagascar, and has been introduced into the Bahamas, Florida and North Australia. In the latter country it now grows like a weed. Before the merits of *Hevea brasiliensis* became firmly established, it was proposed to establish large plantations of *Cryptostegia* in the West Indies, to lop the vine annually and to extract the rubber. It soon became evident, however, that even if the optimistic forecasts were fulfilled, rubber from this plant would cost more to prepare than that from *Hevea*.

With so many genera and species of vines yielding rubber, no single method of collection can be universally applied. In most cases the vine is tapped by making numerous cuts in the stem, the tapper climbing among its twisting branches or cutting and pulling until the main stems can be laid along the ground, where they can be tapped more conveniently. If the latex flows freely, it is collected on leaves or in whatever receptacles are handy. Sometimes the main stem of the vine is severed close to the ground and the vine cut into pieces about 12 inches long, from which the latex is drained and the rubber left in the bark separated by beating and pounding. Vines may be tapped about twice a year and yield from 1 to 4 ounces of rubber per annum. Up to nearly 0.5 pound has been obtained in some instances. In the case of some vines such as *L. owariensis*, the latex is in some areas rather thick and less than half is removed by cutting and draining, so the yield of rubber is greatly increased by beating the bark. On the other hand, the latex of *Clitandra arnoldiana* drains almost completely from the cut stem. These points are of importance because the first consideration is to obtain as much rubber as possible as quickly as possible, and the lopping, draining and beating method of extraction appears to be the most promising.

Preparation of rubber.—With such a wide variety of plants yielding latices markedly different in chemical composition and structure, there is no single method of treatment which can be recommended in all circumstances. The bulk of the latex-yielding trees and plants are found in forests and jungles where direct European supervision is impossible, and are being tapped by a generation of natives who have never known the technical and commercial tricks of the rubber trade. Some of the Europeans now devoting their attention to the subject are on unfamiliar ground and may know little about the technical importance of cleanliness, the evil effects of copper, manganese or exposure to the sun. Rolling or washing machines are not generally available. Methods of producing coagulation are described in technical books which are not well known today and are not easily obtained. The natives may have to rely on an older generation for their information on this subject. There seems little doubt that in many cases rubber collectors and shippers will have to feel their way. Technical experts are being made available, however, and there should be a rapid improvement in quality as experience is gained.

The latex of *Funtumia elastica* is characterized by its remarkable stability. The fresh latex is not coagulated by acids, and can be kept for a long time without the addition of a preservative, although changes in the nonrubber substances do occur, and it is known that the longer the latex is kept the easier

it is to coagulate. The reason for the remarkable stability is not known. The rubber particles are stated to be smaller and more uniform than in *Hevea* latex, but the stability cannot be greatly affected by this, and must be associated with the nature of the nonrubber substances at the surface of the particles.

One of the methods of coagulation employed is to keep the latex in shallow trays of soft wood which absorb serum and allow rapid evaporation, so coagulation occurs in a few days. A similar method which takes much longer is to pour the latex into a hole in the ground lined with clay and allow it to remain there for about 6 weeks, covered with leaves to keep out the dirt. Rubber was frequently prepared in this way in West Africa and marketed in the form of lumps which, of course, contain large amounts of moisture. It is probable that the same method will be used again.

A more usual method of preparing rubber from *Funtumia* latex is to dilute the latex and heat it in an earthenware pot over a slow fire, or to add the latex to boiling water, when a flocculent mass rises to the surface and is collected by hand, or on a stick or scoop. This is either sold as lumps or is cut into strips and dried and wound into a large ball. Coagulation by boiling is also employed on plantations where the coagulum is afterwards rolled into sheet and thoroughly washed. There is obviously considerable risk of damaging the rubber by overheating, and the method is reputed to give rise to tacky rubber.

Some natives employ a hot infusion of the leaves of certain plants to accelerate coagulation, the active coagulating agent being a mixture of tannic and organic acids.

In 1908, one of the native chiefs discovered that *Funtumia* latex could be coagulated without heat by adding the juice of the Diecha vine (*Strophanthus preussii*). This rubber could be made into sheets, lumps or twists.

Attempts have been made to find chemical coagulants, and tannic acid, mercuric chloride, formalin and alum have been recommended, sometimes in association with a little acetic acid, but it is still necessary to dilute the latex with water and to raise the temperature to obtain a coherent clot. It has also been proposed to dilute the latex, allow it to cream, and obtain a coherent clot by pressure. This method takes about a week to separate the rubber from the latex. Any one of these methods may have been employed to prepare the *Funtumia* rubber now being marketed, except that pure chemicals are not likely to be generally available, and mercuric chloride can be definitely ruled out as a commercial coagulant. There will be a definite tendency, however, for all the rubber in a certain area to be prepared by the same method and to appear on the market in a special form. That is the reason why, in the old days, African rubbers were graded according to port of origin and Ivory Coast niggers, *i.e.*, balls, for instance, had a better reputation and commanded a higher price than Lagos niggers.

As there are more than 20 different species of *Landolphia* vine in addition to several species of *Clitandra*, *Carpodinus* and other genera, and as every tribe and village used to have their own ideas as to the best method of preparing rubber, it may be grossly misleading to refer to only a few, which embrace the preparation of balls, slabs, bracelets, niggers, twists, thimbles, cubes, lumps, biscuits, etc. Vine latex can usually be coagulated by heat, particularly that obtained from various species of *Clitandra*. Chemical coagulants can also be employed, such as acetic acid or acid plant juices, and are used for the coagulation of the free flowing latex of some of the *Landolphia* species. Common salt is also sometimes employed. Some *Landolphia* latices

coagulate on diluting with water and standing for a short time. The coagulum is then pressed into the required shape and left to dry. Sometimes the coagulum is rolled into sheet, or stamped into sheet by placing the coagulum between leaves and dancing on it. These sheets are made into cubes or cut into strips and wound into balls or into twists, according to the fashion in the district. In some villages the tappers cover their bodies with latex and by the time they return home it is reasonably dry and the rubber can be pulled off and rolled into balls or twists. In a properly organized industry it might be possible to arrange that all vine latex which flows sufficiently freely to be collected in receptacles should be coagulated with acetic or formic acid and then rolled into sheet, but this is not possible in the short time available.

Both *Funtumia* and vines yield an appreciable amount of latex, which remains on the cut and is there allowed to dry. The rubber is pulled off into strips and is then wound into balls or into some other less usual shape. The vine *L. owariensis* is a fairly common one. In some districts the latex of this vine flows freely and is collected into cups, but in others it is thick and is allowed to coagulate on the cut. Sometimes a tapper cuts a vine and then smears the wound with a coagulant, such as salt or acid juice, to induce coagulation on the plant.

An appreciable amount of root rubber has been prepared by tearing up the long underground stems which grow under some conditions. The stems are dried in the sun to induce coagulation of the latex and then cut into short pieces, from 6 to 12 inches long, which are made into bundles and the bark removed either by pounding dry or by soaking in water for two days before pounding. The separated bark is then more thoroughly dried in the sun and beaten again until the rubber masses together and as much as possible of the bark has been removed. The rubber is then placed in hot water and afterwards beaten again to remove more bark, and the treatment is repeated until the desired degree of cleanness has been achieved. The material is finally softened in hot water and pressed into balls or cylinders.

A similar treatment is applied to the above-ground stems of some vines which contain an appreciable amount of latex after bleeding has finished.

Machines have been proposed and tried in the past for the mechanical separation of rubber from roots and stems, but they never became popular in Africa.

Cleanness.—When the wild rubber arrives in this country it is divided into two main grades, consisting of reasonably clean rubber and material which requires washing. The clean rubber is chiefly ribbed sheet from *Funtumia* latex, together with a little blanket crepe, and includes some *Hevea* and a little *Ceara* rubber. Some of the vine rubbers are also fairly clean, but are not properly dry, owing to the form in which they are prepared. The rubber which requires washing consists almost wholly of *Funtumia* and vine rubber, much of which is labelled with a local or trade name which covers a range of indefinite botanical sources. Red Congo, for instance, is stated to be obtained from four species of *Landolphia*, namely, *owariensis*, *droogmansiara*, *gentilii* and *klainii* and Black Congo from the *Clitandra* species *arnoldiana* and *nzunde*. Consignments of Black Congo have, however, arrived labelled Kikxia, which is the old name for *Funtumia*.

The usual loss in weight of rubber which obviously requires washing is between 10 and 20 per cent, the bulk of which is moisture; the rest is bark, sand, earthy impurities and water-soluble material. In extreme cases, the

TABLE 1

COMPOSITION OF WASHED DRY RUBBER

Origin	No. of samples	Acetone-soluble (per cent)	Ether-soluble in acetone extract (per cent)	Acid value of ether-soluble (mg. per cent)	Acid value of ether-insoluble (mg. per cent)	Nitrogen in extracted rubber (per cent)	Ash in extracted rubber (per cent)
Hevea	17	1.7 to 4.2	1.5 to 3.2	35 to 302	6 to 97	0.21 to 0.56	0.3 to 2.3
Funtumia	15	6.5 to 8.8	6.4 to 8.3	25 to 222	nil	0.4 to 1.5	0.2 to 1.9
Ceara	3	4.2 to 4.5	3.4 to 4.3	46 to 165	...	1.3	1.4 to 3.8
Landolphia							
French and Belgian Congo	9	5.0 to 5.8	3.4 to 4.5	49 to 56	nil	0.01 to 0.09	0.8 to 2.0
Portuguese Guinea	8	5.2 to 7.1	3.9 to 4.6	34 to 105	nil	0.04 to 0.23	2.0 to 6.8
East Africa	5	6.4 to 11.5	3.7 to 8.6	27 to 59	nil	0.11 to 0.21	0.5 to 2.7
Sierra Leone	3	5.7 to 8.1	4.1 to 7.7	43 to 133	nil	0.01 to 0.11	0.2 to 0.6
Nigeria	1	6.0	3.1	37	18	0.4	0.2
French Guinea	1	5.5	3.9	29	nil	0.2	7.1
Chlandra							
Black Congo rubber	9	7.3 to 9.7	6.5 to 7.8	26 to 78	nil	0.3 to 0.5	0.3 to 1.0
Root rubber							
Angola	6	5.2 to 6.8	5.0 to 6.4	56 to 72	nil	0.09 to 0.25	1.0 to 7.4
French and Belgian Congo	5	4.2 to 5.2	3.8 to 4.9	43 to 86	nil to 23	0.09 to 0.16	2.2 to 7.7
Unclassified							
Nigeria	3	3.6 to 14.9	...	15 to 466	...	...	...
French Equatorial Africa (*Caoutchouc sylvestre*)	1	5.6	4.7	108	...	0.5	0.3
Angola	1	6.7	3.2	35	nil	0.09	1.4

washing loss may be over 40 per cent. As dirty rubber is washed at selected depots before distribution, washing losses are not of direct importance to the manufacturer, who can expect to receive his rubber in a reasonably clean and dry condition in the form of dark crepe, possibly massed into a solid lump and perhaps labelled with some trade name which is not very helpful with regard to botanical source. The geographical origin of the rubber is generally known from the markings on the packages, but the botanical source is frequently not indicated, and it may be necessary to obtain further information from an acetone extract or visual examination. *Funtumia* sheet, for example, becomes white when stretched between the fingers, and after a little experience it should be possible to distinguish between *Hevea* and *Funtumia* with reasonable reliability.

Chemical analysis.—It is not easy to determine without doubt the botanical source of the rubber by chemical analysis. Table 1 shows the range of values obtained for different species of rubber. The amount of acetone-soluble non-rubber substances is usually 3 or 4 per cent for *Hevea*, about 8 per cent for *Funtumia* and *Clitandra*, 4 or 5 per cent for *Cearak* and 5 or 6 per cent for *Landolphia*. The character of the extract also differs from one species to another. *Hevea*, for example, may be recognized by the ready solubility in alcohol or water of the fraction of the extract insoluble in ether, and its small but definite acidity. For most wild rubbers the ether-insoluble fraction of the extract is difficult to dissolve in solvents, and only occasionally is slightly acidic. Nearly all the acetone extract of *Funtumia elastica* and *Clitandra* is soluble in ether, while the ether-soluble portion is relatively smaller among *Landolphia* species. Nitrogen values are another guide to the nature of the rubber, being particularly high, often over 1 per cent for *Funtumia* and *Ceara*, about 0.4 per cent for *Clitandra*, and less than 0.2 per cent for *Landolphia* and root rubbers. The latter frequently have a high content of mineral substances.

TABLE 2

PLASTICITY, D.10 VALUE (THICKNESS IN MM. OF SPHERE 0.4 G. AFTER COMPRESSION FOR 10 MIN. AT 100° C UNDER LOAD OF 5 KG.)

Rubber	*Hevea*	*Funtumia*	*Landolphia*	*Clitandra*	*Ceara*
No. of samples examined	300	7	16	7	1
Range	1.55–2.40	1.12–1.77	0.84–1.78	0.92–1.62	1.34
Average	1.68	1.37	1.35	1.34	...

Plasticity.—The fact that the rubber is wet and dirty before treatment is a sign of crude preparation, and it is not surprising that such rubber is sometimes distinctly tacky in patches and, after washing and drying, increases in tackiness at an alarming rate. On the other hand, much of the African wild rubber is of fair quality. It is important, however, to separate good and poor material and a system of grading according to plasticity is under consideration, the grading to be applied to the washed dry rubber before it is distributed to manufacturers. Material which has been adulterated with resinous latices tends to be plastic, particularly in the neighborhood of 100° C, as does also material which deteriorates quickly. The most plastic grade contains the lowest qualities of African rubber and the least plastic grade contains the best. In Table 2 are shown the range of plasticities of different types of African rubbers which are, on the whole, distinctly softer than *Hevea* rubber.

Vulcanization.—In standard fairly pure mixings, using mercaptobenzothiazole or diphenyl guanidine as accelerators, African rubbers may be broadly

divided into two groups: (1) *Hevea, Funtumia, Ceara, Clitandra* and a few species of *Landolphia* such as *L. kirkii* and *ugandensis*, which vulcanize normally when well prepared and only require minor adjustments to the mix to produce good results, and (2) most *Landolphia* species, *e.g.*, Red Congo rubber, and particularly root rubbers, which require much more powerful acceleration before becoming vulcanized, but which then produce good results.

A standard mix used for testing *Hevea* rubber is as follows: Mix A. rubber 100, zinc oxide 6, sulfur 3.5, stearic acid 0.5, mercaptobenzothiazole 0.5.

The rate of cure of *Hevea* rubber in this mix is affected by several factors, among which is the amount of fat acids in the rubber. Fat acids are not present to any marked extent in *Funtumia* or vine rubbers. The ether-soluble acids in *Funtumia*, which may be considerable, are stated to be of a balsamic nature, *e.g.*, benzoic and cinnamic types, and these may not be helpful to vulcanization with mercaptobenzothiazole.

Funtumia rubbers are therefore tested in mix B, which is mix A containing 1.5 parts of stearic acid in place of 0.5 part. Tables 3 and 4 give some results obtained with *Hevea* and *Funtumia* rubbers in the two mixes. The results given by a sample of *Ceara* scrap in mix B are included also.

TABLE 3

VULCANIZATION OF *Hevea* RUBBER IN MIX A
Cure:—60 min. at 127° C

Description	Ether-soluble acid value (mg. KOH)	Tensile strength (kg. per sq. cm.)	Modulus at 700 per cent elongation (kg. per sq. cm.)	Elongation at break (per cent)
Sheet scrap	173	156	130	748
Cameroon strings	56	37	...	695
Rough sheet	83	68	50	760
Sheet strips	176	106	...	685
Uganda scrap	161	92	72	755
Thick sheet	35	65	42	805

TABLE 4

VULCANIZATION OF *Hevea* AND *Funtumia* RUBBERS IN MIX B

Description Origin Form	Ether-soluble acid value (mg. KOH)	Tensile strength (kg. per sq. cm.)	Modulus at 700 per cent elongation (kg. per sq. cm.)	Elongation at break (per cent)
Hevea				
Thick sheet	35	97	83	745
Sheet scrap	142	145	119	745
Bark scrap	101	91	51	815
Cup scrap	99	171	...	690
Funtumia				
Sheet A	117	142	125	750
Sheet B	64	120	61	840
Sheet C	108	110	45	885
Sheet D	222	118	45	881
Sheet E	55	127	113	725
Rough sheet A	25	57	24	860
Rough sheet B	42	108	37	903
Lump	110	131	82	820
Naturally coagulated slab	93	110	40	870
Ceara scrap	165	187	170	740

Hevea rubbers are also tested in a mix of the following composition (Mix C): Rubber 100, zinc oxide 6, sulfur 2.75, diphenylguanidine 0.4. Two samples of

Funtumia sheet showed a considerable difference in modulus at 700 per cent, one being curing slowly. In a mix containing both accelerators, however, this sample vulcanized to a strong and tough rubber. The composition of this Mix D is as follows: Rubber 100, zinc oxide 5, sulfur 2.5, stearic acid 0.5, mercaptobenzothiazole 0.25, diphenylguanidine 0.2.

Some results obtained with *Hevea* and *Funtumia* rubber in mixes C and D are given in Table 5.

TABLE 5

VULCANIZATION OF *Hevea* AND *Funtumia* RUBBERS

Description	Mix	Cure (min. at 141° C)	Tensile strength (kg. per sq. cm.)	Modulus at 700 per cent elongation (kg. per sq. cm.)	Elongation at break (per cent)
Hevea thick sheet	C	60	20	...	650
" sheet scrap	C	60	145	90	800
" bark scrap	C	60	77	46	795
" cup bark	C	60	122	78	785
" Uganda scrap	C	60	93	57	810
Funtumia sheet A	C	60	46	21	855
" " C	C	60	108	46	895
" " B	C	20	179	112	810

The vulcanization of vine and root rubbers in Mix B is shown in Table 6 and in Mix C in Table 7.

TABLE 6

VULCANIZATION OF VINE AND ROOT RUBBERS IN MIX B
Cure:—60 min. at 127° C

Description	Tensile strength (kg. per sq. cm.)	Modulus at 700 per cent elongation (kg. per sq. cm.)	Elongation at break (per cent)
Landolphia			
L. kirkii	76	32	858
L. ugandensis A	100	63	785
" " B	135	56	848
French and Belgian Congo	5 to 53	2 to 28	840 to 1,107
Portuguese Guinea	23 to 90	8 to 23	922 to 1,034
Gold Coast ball	35	7	1,100
Sierra Leone pat	24	8	995
" " ball	15	8	891
Mozambique ball A	5	3	975
" " B	43	9	1,010
Clitandra			
Black Congo	61 to 117	20 to 40	914 to 965
Root rubber	16	6	860

TABLE 7

VULCANIZATION OF VINE AND ROOT RUBBERS IN MIX C
Cure:—60 min. at 141° C

Description	Tensile strength (kg. per sq. cm.)	Modulus at 700 per cent elongation (kg. per sq. cm.)	Elongation at break (per cent)
Landolphia			
L. ugandensis A	93	30	950
" " B	62	17	985
French and Belgian Congo and Portuguese Guinea	nil to 72	13	1,032
Clitandra			
Black Congo	77 to 118	26 to 43	860 to 882
Root rubber		no vulcanization	

Thus, with the exception of Black Congo rubber, which vulcanized well to rather soft vulcanizates, and of a few *Landolphia* species, *e.g.*, *L. kirkii* and *L. ugandensis*, vine and root rubbers are much undervulcanized at normal curing times in standard mixes containing medium accelerators. Even in Mix D, which proved satisfactory for slow-curing *Funtumia* rubber, no marked improvement was obtained, but slow-curing *Landolphia* rubbers from Portuguese Guinea and the French and Belgium Congo vulcanized well in a similar mix (Mix E) containing double the accelerator, *viz.*: rubber 100, zinc oxide 5, sulfur 4, stearic acid 0.5, mercaptobenzothiazole 0.5, diphenylguanidine 0.4.

TABLE 8

VULCANIZATION OF *Landolphia* AND ROOT RUBBERS IN STOCKS CONTAINING MIXED ACCELERATORS

Description	Mix	Tensile strength (kg. per sq. cm.)	Modulus at 700 per cent elongation (kg. per sq. cm.)	Elongation at break (per cent)
Landolphia				
French and Belgian Congo	D	89 to 112	18 to 22	1,045 to 987
" " " "	E	144	88	785
" " " "	F	125	114	715
Portuguese Guinea	D	44 to 74	8 to 17	1,105 to 955
" "	E	164	162	705
" "	F	117 to 153	97 to 136	685 to 755
Root rubber	D	67	19	935
" "	F	106	85	735

Root rubber is generally even more difficult to vulcanize than other *Landolphia* and many experiments were made with different combinations of sulfur, accelerator and stearic acid. The best vulcanization was effected in a mix (Mix F) containing rubber 100, zinc oxide 5, sulfur 1.0, stearic acid 1.5, mercaptobenzothiazole 0.75, tetramethylthiuram disulfide 0.5. Some results for *Landolphia* and root rubber in mixes containing mixed accelerators are given in Table 8. Mixes D and E were vulcanized for 20 minutes at 141° C, and Mix F for 60 minutes at 127° C.

The results given above are not necessarily the best obtainable, and may be improved by the choice of different mixes and vulcanization conditions, but nevertheless they serve to show that slow-curing vine and root rubbers may give well vulcanized, strong products under selected conditions.

A few samples of African rubber have been tested in a tire tread mix of the following composition: rubber 100, zinc oxide 5, sulfur 3, stearic acid 2, mercaptobenzothiazole 1, Micronex gas black 50, and in each case the natural

TABLE 9

BEHAVIOR OF AFRICAN RUBBERS IN A TIRE TREAD MIX

Time of cure (min.)	30	60	90	30	60	90	30	60	90
Description	Tensile strength (kg. per sq. cm.)			Modulus at 300 per cent elongation (kg. per sq. cm.)			Elongation at break (per cent)		
Smoked sheet *Hevea* control	154	203	132	81	100	103	455	420	370
Conakry sheets and strings	...	...	151	...	...	116	...	...	374
Congo nuts and cubes	166	147	144	63	79	84	570	458	440
Funtumia sheets	172	178	165	120	133	139	454	403	364
Funtumia lump	136	...	...	59	...	...	491	...	...
Angola root rubber	...	...	120	...	...	109	...	...	329
Landolphia ugandensis	...	181	...	...	93	...	...	514	...

deficiency of fat acids was compensated for by the addition of the appropriate amount of stearic acid. The cures were 30, 60, 90 minutes at 134° C, and the results are shown in Table 9. They show that the remarkable behavior of African rubber in a pure mix is not a guide to its behavior in one which is heavily loaded with carbon black. It may be accidental that the *Hevea* sample has given the best tensile strength result, and there is still a wide variation in vulcanizing properties, but there is a tendency for the African rubbers to move towards the *Hevea* range of properties.

A practical corollary of these experiments on the vulcanization of African rubber is that a manufacturer would be wise to average his supplies of wild

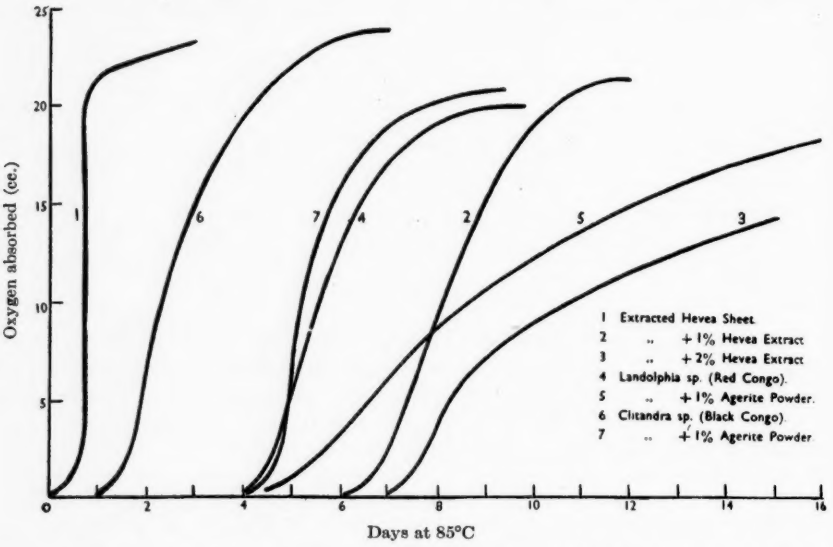

FIG. 1.—Oxygen absorption of Red Congo and Black Congo Rubbers at 85° C, in the form of thin films approximately 0.09 mm. thick and 50 mg. in weight.

rubber as far as possible. In addition he should compensate for deficiency in natural fat acids and, if necessary, adjust his mixes; for instance, by using more powerful accelerators to ensure proper vulcanization. This latter recommendation applies, however, only to mixes containing high proportions of rubber, and may not be necessary for loaded mixes containing carbon black.

The results so far obtained refer to the use of wild rubber alone, but most manufacturers will prefer to use mixtures of this rubber and *Hevea*. In a single experiment in which 20 per cent of slowly-vulcanizing root rubber was mixed with *Hevea* in a pure mix, the vulcanization of the rubber was definitely retarded, and the vulcanized material was reduced in strength.

Aging.—The most difficult and unsatisfactory feature of wild rubber is its aging properties before vulcanization. *Hevea* rubber sometimes keeps forty years without obvious signs of deterioration, and it is poor material which keeps only five years, whereas washed and dry wild rubber may become tacky and resinous in spots within a few weeks. None of these samples contained copper or manganese in an amount greatly in excess of that normally found in *Hevea* rubber.

The rate of oxygen absorption of unvulcanized wild rubber was determined by depositing thin films of definite thickness from benzene solution, drying off the solvent, exposing to an atmosphere of oxygen at 85° C, and measuring the volume of oxygen absorbed over a period of days. Typical results are shown in Figure 1. All the samples of wild rubber absorb oxygen more rapidly than

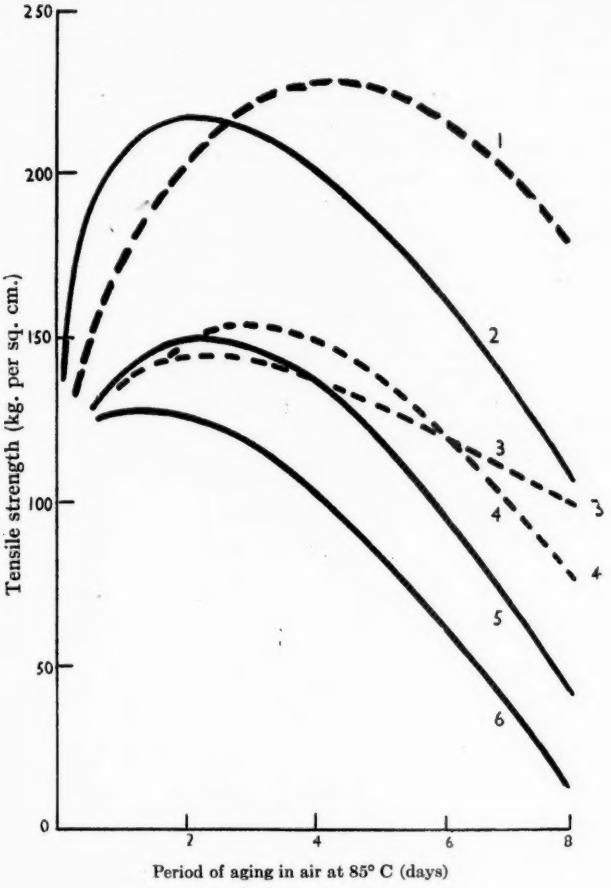

FIG. 2.—Aging of *Funtumia* and *Hevea* Rubber.

1. *Hevea* smoked sheet + antioxidant.
2. *Hevea* smoked sheet.
3. Sheet B + antioxidant.
4. Sheet A + antioxidant.
5. Sheet B.
6. Sheet A.

Hevea, and some of them are markedly inferior. A sample of *Landolphia ugandensis* which became tacky in a few weeks after washing and drying, absorbed oxygen overnight, and was not appreciably improved by the addition of the acetone extract of *Hevea* rubber. Other samples were better than this, and were improved by the addition of Agerite Powder, but they were still inferior to *Hevea*.

Aging results on the vulcanized rubber have so far been obtained only on two samples of *Funtumia* native sheet, vulcanized for different periods in a

mercaptobenzothiazole mix, both with and without antioxygen. The *Funtumia* rubbers were softer and weaker in the mix employed and, in the absence of antioxygen, did not increase so markedly in tensile strength in the early stages of aging at 85° C in air as did the control *Hevea* smoked sheet, or retain as great a proportion of their strength after six days' aging. In the presence of antioxygen, the aging properties of the *Funtumia* rubbers were improved, but the difference between them and *Hevea* was not reduced. On the whole, the *Hevea* rubber has about 50 per cent longer life than *Funtumia*, but comparatively "pure" mixes were used, and the difference between the two types of rubber may not be so marked in technical mixes. The results are given in Figure 2.

Structure of the rubber hydrocarbon.—The tire tread vulcanizates prepared from African rubbers and referred to in the section dealing with vulcanization were tested for hardness and swelling in pool petrol and pure benzene, and the results obtained are shown in Figure 3, plotted against modulus at 300 per cent elongation. The linear relationship obtained for both these values suggests that the rubber hydrocarbon is identical in the rubbers examined, and the ratio between swelling in the two solvents is identical with that in *Hevea*.

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